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(54) OLEFIN POLYMERIZATION CATALYST AND PRODUCTION OF POLYOLEFIN

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polyolefin with high melt tension, resin compatibility and bulk density.

SOLUTION: This polyolefin is obtained by the following two steps: first, in the presence of a catalyst comprising (A) at least two kinds of compound selected from group 4 transition metal compounds each bearing cyclopentadienyl group and (B) (B-1) an aluminumoxy compound, (B-2) an ionic compound capable of converting the transition metal compounds to the corresponding cations through reaction therewith and (B-3) at least one kind of substance selected from clay, clay mineral and layered compounds of ion exchanging capability, at least one kind of compound selected from 2-20C α -olefins and cyclic olefins is prepolymerized in an amount of 0.01-2,000 g per g of the transition metal compounds to form a prepolymerization catalyst with an intrinsic viscosity $[\eta]$ of 0.01-20 dL/g. Next, at least one kind of compound selected from 2-20C α -olefins, cyclic olefins and styrene-based monomers is polymerized or copolymerized in the presence of the above prepolymerization catalyst (plus an organoaluminum compound).

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CLAIMS

[Claim(s)]

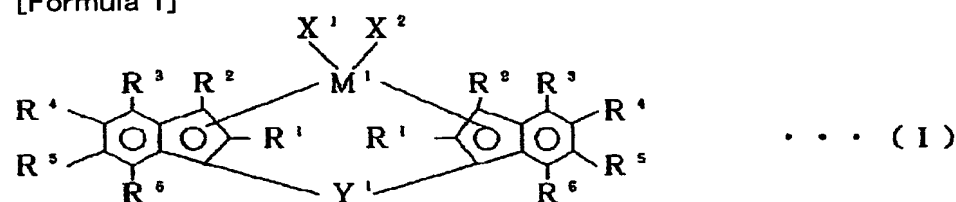
[Claim 1] (A) At least two sorts chosen from the transition-metals compounds of the 4th group of the periodic table who has a cyclopentadienyl group, (B) (B-1) Under existence of the catalyst which was chosen as the ionicity compound list which reacts with an aluminum oxy compound and the above-mentioned (B-2) transition-metals compound, and can be changed into a cation from clay (B-3), the clay mineral, and the ion-exchange nature stratified compound and which comes to contain a kind at least, it was chosen out of the alpha olefin and annular olefin of carbon numbers 2-20 -- at least a kind The precuring catalyst characterized by coming to carry out precuring at a per [1g of above-mentioned transition-metals compounds / 0.01-2000g] rate, and being in the range whose limiting viscosity [eta] is 0.01-20 deciliters/g.

[Claim 2] The precuring catalyst according to claim 1 whose catalyst used for precuring is what contains the (C) organoaluminium compound and/or support further.

[Claim 3] (A) The precuring catalyst of a component or the (B) component according to claim 1 with which a kind is supported by support at least.

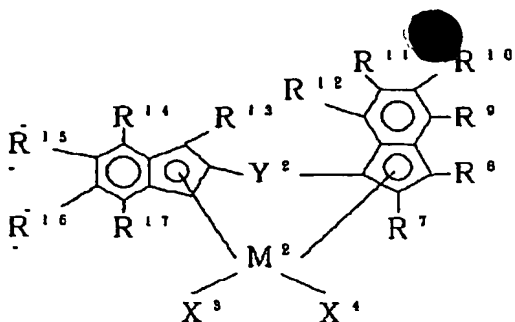
[Claim 4] (A) The transition-metals compound of a component is a general formula (A-1) (I).

[Formula 1]

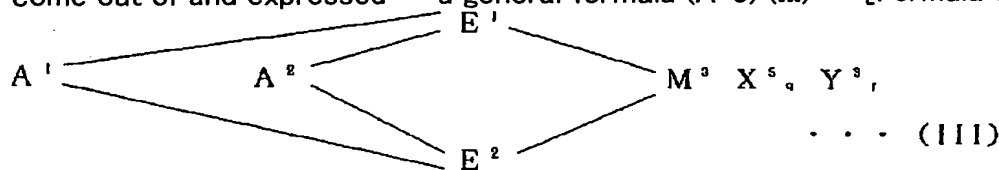


R1 -R6 shows the hydrocarbon group of a hydrogen atom, a halogen atom, and carbon numbers 1-20, or the halogen content hydrocarbon group of carbon numbers 1-20 independently among [type, respectively. R3 R4 and R4 R5 And R5 R6 It may join together mutually and a lot at least may form a ring. inside -- X1 And X2 The hydrocarbon group of a hydrogen atom, a halogen atom, or carbon numbers 1-20 is shown independently, respectively. Y1 the radical of the bivalence which combines two ligands -- it is -- the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, germanium, or a tin content radical -- being shown -- M1 Titanium, a zirconium, or a hafnium is shown.] The transition-metals compound, general formula (A-2) which are come out of and expressed (II)

[Formula 2]



R7 -R13, R15, R16 and X3, and X4 show a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently among [type, respectively, it may join together mutually and R7 and R8 may form a ring. R14 and R17 show a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently, respectively. Y2 It is the radical of the bivalence which combines two ligands. The hydrocarbon group of carbon numbers 1-20, The halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, a germanium content radical, - O-, -CO-, -S-, -SO2-, -NR18-, --18-, -P(O) R18-, -BR18-, or -AlR18- is shown, and R18 shows a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, and the halogen content hydrocarbon group of carbon numbers 1-20. M2 Titanium, a zirconium, or a hafnium is shown.] the transition-metals compound and list which are come out of and expressed -- a general formula (A-3) (III) -- [Formula 3]



M3 shows titanium, a zirconium, or a hafnium among [type. E1 And E2 It is the ligand chosen from a substituent cyclopentadienyl group, an indenyl group, a permutation indenyl group, a hetero cyclopentadienyl group, a permutation hetero cyclopentadienyl group, the amide group, the phosphide radical, the hydrocarbon group, and the silicon content radical, respectively. A1 And A2 It minds and the structure of cross linkage is formed, and even if they are mutually the same, you may differ. X5 the ligand of sigma bond nature -- being shown -- X5 the case where there are more than one -- two or more X5 even when it is the same -- differing -- **** -- other X5, E1, and E2 Or Y3 The bridge may be constructed. Y3 a Lewis base -- being shown -- Y3 the case where there are more than one -- two or more Y2 even when it is the same -- differing -- **** -- other Y3, E1, and E2 Or X5 constructing a bridge -- **** -- A1 And A2 The bridge formation radical which consists of a with a carbon numbers of one or more hydrocarbon group, respectively is shown, and even if they are mutually the same, they may differ. q shows [(valence of M3) -2] for the integer of 1-5, and r shows the integer of 0-3.] The precuring catalyst according to claim 1 to 3 which is at least two sorts which came out and were chosen from the transition-metals compound expressed.

[Claim 5] (A) The precuring catalyst according to claim 1 to 4 whose transition-metals compound of a component is the thing to choose from a zirconium compound-hafnium compound, a zirconium compound-zirconium compound, and a hafnium compound-hafnium compound, and which shifts and consists of that combination.

[Claim 6] The catalyst for olefin polymerization which consists of a precuring catalyst and an organoaluminium compound according to claim 1 to 5.

[Claim 7] The manufacture approach of the polyolefine which was chosen from the alpha olefin of carbon numbers 2-20, the annular olefin, and the styrene monomer under existence although the organoaluminium compound was added to the bottom of existence of a precuring catalyst

according to claim 1, or this precuring catalyst and which is characterized for a kind by the polymerization or copolymerizing at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the manufacture approach of polyolefine, in more detail, melting tension of this invention is high, it is excellent in resin phase solubility, and relates to the approach of manufacturing the high polyolefine of bulk density cheaply and efficiently.

[0002]

[Description of the Prior Art] Polyolefine is broadly used in many fields taking advantage of the outstanding property. However, in the conventional polyolefine, melting tension and melting viscoelasticity ran short, the phenomenon of drawdown tended to happen to **** inferior to the stability of the parison in large-sized blow molding, and shaping of large-sized components was difficult. Moreover, in order to raise melting tension, when macromolecule quantification is carried out, a melting fluidity falls and the problem of being inapplicable to shaping of a complicated configuration arises.

[0003] Moreover, in the field of a foaming object, although the demand to the foaming object which has thermal resistance with lightweight-izing, adiathermic, damping nature, etc. increases and the polypropylene nature foaming object is expected, what the foaming object melting tension is insufficient and it may fully be satisfied with conventional polypropylene of an object is hard to be acquired from is the actual condition. In order to make the field of the invention of this polypropylene expand further, extrusion-molding workability needs to be improved. The approach of improving melting workability, the method of making polyolefine construct a bridge selectively and improving melting workability, etc. are tried by making variously the attempt which is going to improve the melting workability of polyolefine, for example, improving the polymerization catalyst and polymerization formula at the time of manufacture of polyolefine, and expanding the molecular weight distribution conventionally.

[0004] On the other hand, in the ethylene system polymer, although a molecular weight distribution is narrow, the ethylene system polymer with which melting tension was improved is proposed by the catalyst system which combined a metallocene catalyst, aluminoxane, etc. recently (JP,4-213306,A). Moreover, also about the ethylene system polymer manufactured according to a restricted geometry mold catalyst, although molecular weight distribution are narrow similarly, it is indicated that melting tension is improved (JP,3-163088,A) and existence of long-chain branching is suggested. However, the improvement in extrusion-molding workability is still small by the improvement in melting tension. Moreover, although melting tension is [resin / polystyrene system / polyethylene system resin or a polypropylene resin] high, in the sheet forming of deep drawing etc., it is still deficient in performance.

[0005] Although a melting working characteristic will generally improve by the branching if long-chain branching is introduced into a polymer chain, it is the so-called composite-material field which consists of a different-species polymer in the branched polymer which constituted branched chain from a different monomer from a principal chain polymer, and it is possible to reduce the boundary tension between different-species polymers, to raise the dispersibility of a polymer, and to give effectively physical properties which can be easily incompatible, such as impact strength and rigidity. Moreover, since micro phase separation structure is taken, the

application to various elastomers is also possible. However, since introducing branching had a limit in the polyolefine field until now, there was a limitation of application expansion. If this becomes possible, the application field is expected to expand greatly from the outstanding machine physical properties which polyolefine originally has, and the environmental compatibility represented by recycle nature.

[0006] by the way, as an approach of improving the melting tension of polyolefine and raising a melting working characteristic How to mix the high density polyethylene of the amount of giant molecules with high (1) melting tension until now (JP,6-55868,B), (2) How to mix high density polyethylene with the high melting tension manufactured according to a chromium system catalyst (JP,8-92438,A), (3) How to mix the low density polyethylene manufactured by the general high voltage radical polymerization method, (4) How to raise melting tension to common polyolefine by carrying out an optical exposure, (5) How to raise melting tension to common polyolefine by carrying out an optical exposure under existence of a cross linking agent and a peroxide, (6) The approach of carrying out the graft of the radical polymerization nature monomers, such as styrene, to common polyolefine, the approach (JP,5-194778,A, JP,5-194779,A) of carrying out copolymerization of (7) olefins and the polyene, etc. are tried.

[0007] However, in the approach of aforementioned (1) - (3), since the elastic modulus of the component which heightens melting tension, reinforcement, and thermal resistance run short, it does not escape polyolefine and that the description of polypropylene original especially is spoiled. Moreover, in the above (4) and the approach of (5), when it is difficult to control the crosslinking reaction which occurs as side reaction and an adverse effect arises in a poor appearance and a mechanical characteristic according to generating of gel, a limitation is to control fabricating-operation nature to arbitration, and there is a problem that a control range is narrow. Furthermore, in the approach of the above (6), a problem is produced in generating and the manufacturing cost of gel, and in the approach of the above (7), the amelioration effectiveness of melting tension is small, and when sufficient effectiveness is not demonstrated, we are anxious also about generating of gel.

[0008]

[Problem(s) to be Solved by the Invention] Under such a situation, melting tension of this invention is high, it is excellent in resin phase solubility, and aims at offering the approach of manufacturing the high polyolefine of bulk density cheaply and efficiently.

[0009] this invention persons found out melting tension being high a polymerization or by copolymerizing, excelling an alpha olefin, an annular olefin, or a styrene monomer in resin phase solubility, and the polyolefine which has properties, like bulk density is high being obtained, and attaining the object under existence of the precuring catalyst which is made to carry out precuring of the olefin to the bottom of existence of a specific catalyst, and is acquired, as a result of repeating research wholeheartedly, in order to attain the above-mentioned object. This invention is completed based on this knowledge.

[0010] Namely, at least two sorts as which this invention was chosen from the transition-metals compounds of the 4th group of the periodic table who has the (A) cyclopentadienyl group, (B) (B-1) Under existence of the catalyst which was chosen as the ionicity compound list which reacts with an aluminum oxy compound and the above-mentioned (B-2) transition-metals compound, and can be changed into a cation from clay (B-3), the clay mineral, and the ion-exchange nature stratified compound and which comes to contain a kind at least, it was chosen out of the alpha olefin and annular olefin of carbon numbers 2-20 -- at least a kind The precuring catalyst characterized by coming to carry out a polymerization at a per [1g of above-mentioned transition-metals compounds / 0.01-2000g] rate, and being in the range whose limiting viscosity [η] is 0.01-20 deciliters/g is offered. Moreover, although this invention added the organoaluminium compound to the bottom of existence of this precuring catalyst, or this precuring catalyst, it offers under existence the manufacture approach of the polyolefine which was chosen from the alpha olefin of carbon numbers 2-20, the annular olefin, and the styrene monomer and which is characterized for a kind by the polymerization or copolymerizing at least.

[0011]

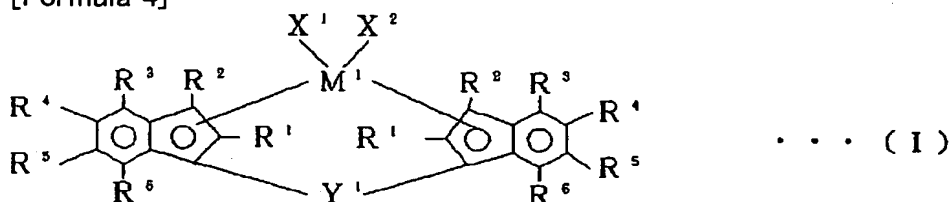
[Embodiment of the Invention] A kind chosen as a catalyst used for precuring in the manufacture

approach of this invention from the transition-metals compounds of the 4th group of the periodic table who has the (A) cyclopentadienyl group, (B) (B-1) The thing which was chosen as the ionicity compound list which reacts with an aluminum oxy compound and the ((B-2) A) above-mentioned transition-metals compound, and can be changed into a cation from clay (B-3), the clay mineral, and the ion-exchange nature stratified compound and which contains a kind at least is used. A kind chosen, for example from a component (A-1), a following component (A-2), and (A-3) a following component as a transition-metals compound of the 4th group of the periodic table who has the indenyl group of the above-mentioned (A) component can be mentioned.

(A-1) Component : (A-1) a component is a general formula (I).

[0012]

[Formula 4]



[0013] R1 -R6 shows the hydrocarbon group of a hydrogen atom, a halogen atom, and carbon numbers 1-20, or the halogen content hydrocarbon group of carbon numbers 1-20 independently among [type, respectively. R3 R4 and R4 R5 And R5 R6 It may join together mutually and a lot at least may form a ring, inside -- X1 And X2 The hydrocarbon group of a hydrogen atom, a halogen atom, or carbon numbers 1-20 is shown independently, respectively. Y1 the radical of the bivalence which combines two ligands -- it is -- the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, germanium, or a tin content radical -- being shown -- M1 Titanium, a zirconium, or a hafnium is shown.] It comes out and is the transition-metals compound expressed.

[0014] It sets to a general formula (I) and is R3. R4 and R4 R5 And R5 R6 The inner transition-metals compound with which the lot formed the ring at least is a compound known as a BASF mold complex. It sets to said general formula (I), and is R1 -R6. Chlorine, a bromine, a fluorine, and an iodine atom are mentioned as an inner halogen atom. As a hydrocarbon group of carbon numbers 1-20, for example Alkyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, n-hexyl group, and n-decyl group, The radical which aralkyl radicals, such as aryl groups, such as a phenyl group, 1-naphthyl group, and 2-naphthyl group, and benzyl, etc. were mentioned, and was permuted as a halogen content hydrocarbon group of carbon numbers 1-20 by the halogen atom with one or more pieces suitable for the hydrogen atom of the above-mentioned hydrocarbon group is mentioned. This R1 -R6 The radical which may differ even if mutually the same, and adjoins, i.e., R3, R4 and R4 R5 And R5 R6 A lot at least needs the inner thing for which it joins together mutually and the ring is formed. As an indenyl group in which such a ring was formed, 4, 5-benzoindenyl group, alpha-acenaphtho indenyl group, the alkylation object of the carbon numbers 1-10, etc. can be mentioned, for example.

[0015] Moreover, X1 And X2 Inside, as a halogen atom, chlorine, a bromine, a fluorine, and an iodine atom are mentioned and aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, tert-butyl, and n-hexyl group, and a phenyl group, and benzyl, etc. are mentioned as a hydrocarbon group of carbon numbers 1-20, for example. X1 And X2 It may be mutually the same or you may differ. On the other hand, it is Y1. It is the radical of the bivalence which combines two ligands. As a hydrocarbon group of the bivalence of the carbon numbers 1-20 of them for example, methylene group; -- dimethyl methylene group; -- alkylene groups, such as 1, 2-ethylene; dimethyl -1, 2-ethylene; 1, 4-tetramethylen radical; 1, and 2-cyclo propylene radical, -- Aryl alkylene groups, such as a diphenylmethylene radical, etc. are mentioned and a chloroethylene radical, a chloro methylene group, etc. are mentioned as a halogen content hydrocarbon group of the bivalence of

carbon 1-20, for example. Moreover, as a silicon content radical of bivalence, a methyl silylene radical, a dimethyl silylene radical, a diethyl silylene radical, a diphenyl silylene radical, a methylphenyl silylene radical, etc. are mentioned, for example. Furthermore, as a germanium content radical and a tin content radical, the radical which changed silicon into germanium and tin can be mentioned in the above-mentioned silicon content radical. In addition, Y1 Although two ligands combined are usually the same, you may change with cases.

[0016] As a transition-metals compound expressed with the general formula (I) of this (A-1) component, the compound indicated by JP,6-184179,A, JP,6-345809,A, etc. can be mentioned, for example. As an example rac-dimethylsilane diyl-bis--1- The 2-methyl -4, (5-benzoindenyl)-zirconium dichloride, rac-phenylmethyl silane diyl-screw -1 -(2-methyl -4, 5-benzoindenyl)-Zirconium dichloride, rac-ethane diyl-bis--1- The 2-methyl -4, (5-benzoindenyl)-zirconium dichloride, rac-butane diyl-screw -1 -(2-methyl -4, 5-benzoindenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- (4 and 5-benzoindenyl)-zirconium dichloride, rac-screw -1 -(2-methyl-alpha-methyl-alpha-acenaphtho indenyl)- Zirconium dichloride, rac-phenylmethyl silane diyl-bis--1- What permuted the zirconium in benzoindenyl molds, such as (2-methyl-alpha-acenaphtho indenyl)-zirconium dichloride, or acenaphtho indenyl mold compounds, and these compounds by titanium or the hafnium can be mentioned.

[0017] Furthermore, it sets to said general formula (I), and a component (A-1) is R3. R4 and R4 R5 And R5 R6 Any group is the transition-metals compound which has 4, 5 and 6 corresponding to the transition-metals compound or it which has the indenyl frame which does not form the ring, and a 7-tetrahydro indenyl frame. This transition-metals compound is a compound known as a Hoechst mold complex. As a transition-metals compound of this (A-1) component, the compound indicated by JP,4-268308,A, a 5-306304 official report, a 6-100579 official report, the 6-157661 official report, the 7-149815 official report, the 7-188318 official report, the 7-258321 official report, etc. can be mentioned, for example.

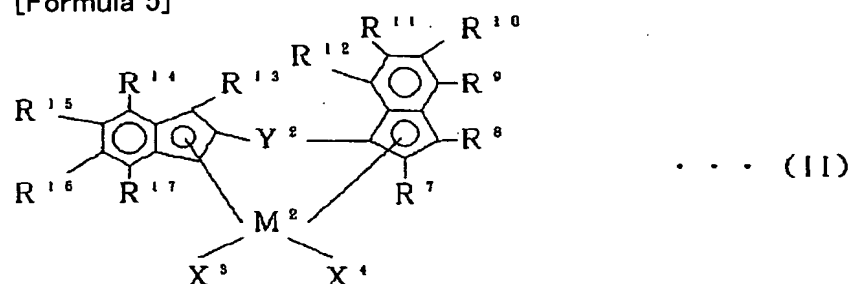
[0018] As an example Dimethylsilane diyl-bis--1- (2-methyl-4-phenyl indenyl)-zirconium dichloride, Dimethylsilane diyl-screw-1-[2-methyl-4- Indenyl]-zirconium dichloride, (1-naphthyl) Dimethylsilane diyl-bis--1- (2-ethyl-4-phenyl indenyl)-zirconium dichloride, dimethylsilane diyl-bis--1-[2-ethyl-4-(1-naphthyl) indenyl] zirconium dichloride, phenylmethyl silane diyl-bis--1- (2-methyl-4-phenyl indenyl)-zirconium dichloride, phenylmethyl silane diyl-bis--1-[2-methyl-4-(1-naphthyl) indenyl]-zirconium dichloride, phenylmethyl silane diyl-bis--1- Aryl substitution products, such as (2-ethyl-4-phenyl indenyl)-zirconium dichloride and phenylmethyl silane diyl-bis--1-[2-ethyl-4-(1-naphthyl) indenyl]-zirconium dichloride, rac-dimethyl silylene-bis--1- (2-methyl-4-ethyl indenyl)-zirconium dichloride, rac-dimethyl silylene-screw -1 -(2-methyl-4-isopropyl indenyl)- Zirconium dichloride, rac-dimethyl silylene-bis--1- (2-methyl-4-tertiary butyl indenyl)-zirconium dichloride, rac-phenylmethyl silylene-screw -1 -(2-methyl-4-isopropyl indenyl)- Zirconium dichloride, rac-dimethyl silylene-bis--1- (2-ethyl-4-methyl indenyl)-zirconium dichloride, rac-dimethyl silylene-screw -1 -(2-methyl-4-ethyl indenyl)- At least 2, such as zirconium dimethyl, and 4- Substitution product, rac-dimethyl silylene-bis--1- (4 and 7-dimethyl indenyl)-zirconium dichloride, rac-1, and 2-ethane diyl - bis--1-(2-methyl -4, 7-dimethyl indenyl)-zirconium dichloride and rac-dimethyl silylene-bis--1- (3 and 4 --) 7-trimethyl indenyl-zirconium dichloride, rac-1 and 2-ethane diyl - bis--1-(4, 7-dimethyl indenyl)-zirconium dichloride, rac-1, and 2-butane diyl - bis--- at least 2, 4, and 7- at least 4, such as -1-(4, 7-dimethyl indenyl)-zirconium dichloride, and 7- At least 3, 4, and 7- Or a substitution product, dimethylsilane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, phenylmethyl silane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, rac-1, 2-ethane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-diphenyl silane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, rac-phenylmethyl silane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- At least 2, such as (2, 4, and 6-trimethyl indenyl)-zirconium dichloride, 4, and 6- is a substitution product and a rac-dimethylsilane diyl-screw. - 1 -(2, 5, 6-trimethyl indenyl)- At least 2, such as zirconium dichloride, 5, and 6- Substitution product, rac-

dimethyl silylene-screw - (2-methyl -4, 5 and 6, and 7-tetrahydro 1-indenyl)-zirconium dichloride, rac-ethylene-screw -(2-methyl -4, 5, 6, 7-tetrahydro-1-indenyl)- Zirconium dichloride, rac-dimethyl silylene-screw - (2-methyl -4, 5 and 6, and 7-tetrahydro-1-indenyl)-zirconium dimethyl, rac-ethylene-screw (2-methyl -4, 5, 6, 7-tetrahydro-1-indenyl)-zirconium dimethyl, rac-ethylene-screw - 4, 5 and 6, such as (4, 7-dimethyl -4, 5 and 6, and 7-tetrahydro-1-indenyl)-zirconium dichloride, a 7-tetrahydro indenyl compound, etc., And what permuted the zirconium in these compounds by titanium or the hafnium can be mentioned.

(A-2) Component : (A-2) a component is a general formula (II).

[0019]

[Formula 5]



[0020] R7 -R13, R15, R16 and X3, and X4 show a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently among [type, respectively, it may join together mutually and R7 and R8 may form a ring. R14 and R17 show a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently, respectively. Y2 It is the radical of the bivalence which combines two ligands. The hydrocarbon group of carbon numbers 1-20, The halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, a germanium content radical, - O-, -CO-, -S-, -SO2-, -NR18-, --18-, -P(O) R18-, -BR18-, or -AlR18- is shown, and R18 shows a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, and the halogen content hydrocarbon group of carbon numbers 1-20. M2 Titanium, a zirconium, or a hafnium is shown.] It comes out and is the transition-metals compound expressed.

[0021] This transition-metals compound is a single bridge formation mold complex. It sets to said general formula (II), and is R7 -R13, and R15, R16 and X3. And X4 Chlorine, a bromine, a fluorine, and an iodine atom are mentioned as an inner halogen atom. As a hydrocarbon group of carbon numbers 1-20, for example Alkyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, n-hexyl group, and n-decyl group, Aralkyl radicals, such as aryl groups, such as a phenyl group, 1-naphthyl group, and 2-naphthyl group, and benzyl, etc. are mentioned. As a halogen content hydrocarbon group of carbon numbers 1-20 The radical permuted by the halogen atom with one or more pieces suitable for the hydrogen atom of the above-mentioned hydrocarbon groups, such as trifluoromethyl, is mentioned. As a silicon content radical, as an oxygen content radical, a methoxy group, an ethoxy radical, etc. are mentioned, a thiol group, a sulfonic group, etc. are mentioned, a trimethylsilyl radical, a dimethyl (t-butyl) silyl radical, etc. are mentioned, and a phenyl phosphine radical etc. is mentioned [a dimethylamino radical etc. is mentioned and] as a Lynn content radical as a nitrogen content radical as a sulfur content radical. Moreover, R7 R8 It may join together mutually and rings, such as a fluorene, may be formed. The radical excluding a hydrogen atom from what was mentioned in the above R7 - R13 grade as an example of R14 and R17 is mentioned. As R7 and R8, a hydrogen atom and a with a carbon number of six or less alkyl group are desirable, a hydrogen atom, a methyl group, an ethyl group, an isopropyl group, and a cyclohexyl radical are more desirable, and a hydrogen atom is still more desirable. Moreover, R9, R12, R14 And as R17, a with a carbon number of six or less alkyl group is desirable, a methyl

group, an ethyl group, an isopropyl group, and a cyclohexyl radical are more desirable, and an isopropyl group is still more desirable. R10, R11, R13, R15 And as R16, a hydrogen atom is desirable. X3 X4 If it carries out, a halogen atom, a methyl group, an ethyl group, and a propyl group are desirable.

group are desirable.

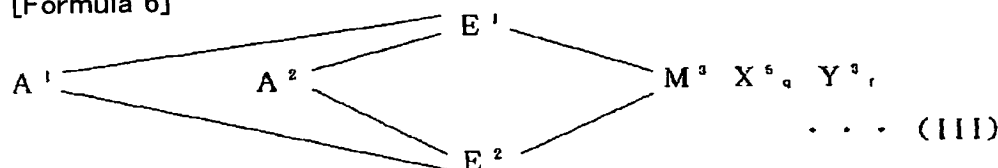
[0022] Y2 As an example, methylene, ethylene, ethylidene, isopropylidene, Cyclohexylidene, 1, 2-cyclo hexylene, dimethyl silylene, Tetramethyl disilylene, dimethylgermirene, methyl BORIRIDEN ($\text{CH}_3\text{-B=}$), Methyl aluminum RIDEN ($\text{CH}_3\text{-aluminum=}$), phenyl HOSUFIRIDEN (Ph-P=), Phenyl phospho RIDEN (PhPO=), 1, 2-phenylene, vinylene (-CH=CH-), There are vinylidene ($\text{CH}_2\text{ =C=}$), methyl imide, oxygen (-O-), sulfur (-S-), etc., and methylene, ethylene, ethylidene, and isopropylidene are desirable in respect of the object achievement of this invention also in these.

MO-5, in which a hafnium is suitable although titanium, a zirconium, or a hafnium is shown.

M2 Especially a hafnium is suitable although titanium, a zirconium, or a hafnium is shown.
[0023] As an example of a transition-metals compound expressed with said general formula (II) 1 and 2-ethane diyl (1- (4, 7-diisopropyl indenyl)) (2-(4, 7-diisopropyl indenyl) hafnium dichloride --) 1 and 2-ethane diyl (9-fluorenyl) (2-(4, 7-diisopropyl indenyl) hafnium dichloride --) isopropylidene (1- (4, 7-diisopropyl indenyl)) (2-(4, 7-diisopropyl indenyl) hafnium dichloride --) 1 and 2-ethane diyl (1- (4, 7-dimethyl indenyl)) (2-(4, 7-diisopropyl indenyl) hafnium dichloride --) 1, 2-ethane diyl (9-fluorenyl) (2- (4, 7-dimethyl indenyl)) hafnium dichloride, Isopropylidene (1- (4, 7-dimethyl indenyl)) (although 2-(4, 7-diisopropyl indenyl) hafnium dichloride etc. can mention what permuted the hafnium in these compounds by the zirconium or titanium) It is not limited to these. In addition, these people can manufacture the transition-metals compound expressed with said general formula (II) by the approach indicated by Japanese Patent Application No. No. 296612 [09 to] which applied previously.

(A-3) Component : (A-3) a component is a general formula (III) [0024].

[Formula 6]



[0025] M3 shows titanium, a zirconium, or a hafnium among [type. E1 And E2 It is the ligand chosen from a substituent cyclopentadienyl group, an indenyl group, a permutation indenyl group, a hetero cyclopentadienyl group, a permutation hetero cyclopentadienyl group, the amide group, the phosphide radical, the hydrocarbon group, and the silicon content radical, respectively. A1 And A2 It minds and the structure of cross linkage is formed, and even if they are mutually the same, you may differ. X5 the ligand of sigma bond nature -- being shown -- X5 the case where there are more than one -- two or more X5 even when it is the same -- differing -- **** -- other X5, E1, and E2 Or Y3 The bridge may be constructed. Y3 a Lewis base -- being shown -- Y3 the case where there are more than one -- two or more Y2 even when it is the same -- differing -- **** -- other Y3, E1, and E2 Or X5 constructing a bridge -- **** -- A1 And A2 The bridge formation radical which consists of a with a carbon numbers of one or more hydrocarbon group, respectively is shown, and even if they are mutually the same, they may differ. q shows [(valence of M3) -2] for the integer of 1-5, and r shows the integer of 0-3.] It comes out and is the transition-metals compound (a duplex bridge formation mold complex may be called hereafter) expressed.

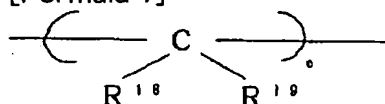
[0026] Said general formula (III) It sets and is M3. Although titanium, a zirconium, or a hafnium is shown, a zirconium and a hafnium are suitable. E1 And E2 above -- respectively -- a substituent cyclopentadienyl group, an indenyl group, a permutation indenyl group, a hetero cyclopentadienyl group, a permutation hetero cyclopentadienyl group, and an amide group (-N -- <) -- >

group, a permutated hetero cyclopentadienyl group, and an amide group (—C(=O)—). The ligand chosen from (however, R is the hydrocarbon group or hetero atom content radical of hydrogen or carbon numbers 1–20) is shown, and it is A1 and A2. It minds and the structure of cross linkage is formed. Moreover, E1 And E2 You may differ, even if mutually the same. This E1 And E2 If it carries out, a substituent cyclopentadienyl group, an indenyl

group, and a permutation indenyl group are desirable.

[0027] Moreover, X3 As an example of the sigma bond nature ligand shown, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20, the aryloxy group of carbon numbers 6-20, the amide group of carbon numbers 1-20, the silicon content radical of carbon numbers 1-20, the phosphide radical of carbon numbers 1-20, the sulfide radical of carbon numbers 1-20, the acyl group of carbon numbers 1-20, etc. are mentioned. this X3 the case where there are more than one -- two or more X3 even when it is the same -- differing -- **** -- other X3, E1, and E2 Or Y2 The bridge may be constructed. On the other hand, it is Y3. Amines, ether, phosphines, thioether, etc. can be mentioned as an example of a Lewis base shown. this Y3 the case where there are more than one -- two or more Y3 even when it is the same -- differing -- **** -- other Y3 E1 and E2 Or X5 The bridge may be constructed. Next, A1 And A2 As a bridge formation radical which consists of a with a carbon numbers of one or more shown hydrocarbon group, it is a general formula [0028], for example.

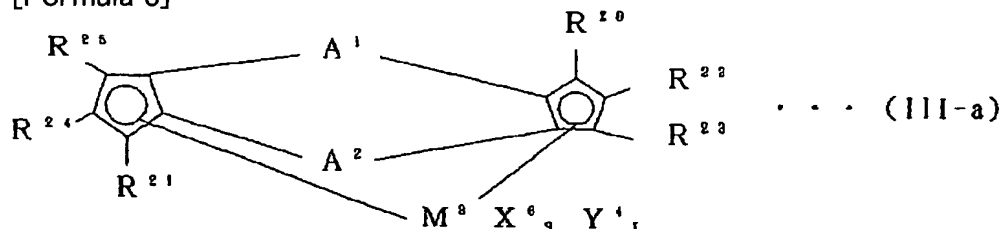
[Formula 7]



[0029] (R18 and R19 are a hydrogen atom or the hydrocarbon group of carbon numbers 1-20, respectively, even if mutually the same, you may differ, and it may join together mutually, and they may form the ring structure.) e shows the integer of 1-4. What is expressed is mentioned and a methylene group, ethylene, an ethylidene radical, a propylidene radical, an isopropylidene radical, a cyclohexylidene radical, 1, 2-cyclohexylene radical, a vinylidene radical ($\text{CH}_2=\text{C}=\cdot$), etc. can be mentioned as the example. In these, a methylene group, ethylene, and an isopropylidene radical are suitable. This A1 And A2 You may differ, even if mutually the same. This general formula (III) It sets to the transition-metals compound expressed, and is E1. And E2 It is A1 when it is a substituent cyclopentadienyl group, an indenyl group, or a permutation indenyl group. And A2 Association of a bridge formation radical may be a duplex ($2(1'1')2'$) bridge formation mold, and may be a duplex ($2(1'2')1'$) bridge formation mold. Such a general formula (III) In the transition-metals compound expressed, it is a general formula (III-a).

[0030]

[Formula 8]



[0031] The transition-metals compound which comes out and makes a ligand the duplex bridge formation mold bis(cyclopentadienyl) derivative expressed is desirable. In the above-mentioned general formula (III-a), M3, A1, A2, and q and r are the same as the above. X6 the ligand of ** sigma bond nature -- being shown -- X6 the case where there are more than one -- two or more X6 even when it is the same -- differing -- **** -- other X6 Or Y4 The bridge may be constructed. This X6 As an example, it is a general formula (III). X5 The same thing as what was illustrated by explanation can be mentioned. Y4 a Lewis base -- being shown -- Y4 the case where there are more than one -- two or more Y4 even when it is the same -- differing -- **** -- other Y3 Or X4 The bridge may be constructed. As this example of Y4, it is a general formula (III). Y3 The same thing as what was illustrated by explanation can be mentioned. Although R20-R25 show a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, or a hetero atom content radical, respectively, at least one of them needs not to be a hydrogen atom. Moreover, even if R20-R25 are mutually the same, they may differ from each other, and adjoining

radicals may join together mutually and they may form the ring.

[0032] The ligands of the transition-metals compound which makes a ligand this duplex bridge formation mold bis(cyclopentadienyl) derivative may be any of a duplex (2 (1 1') 2') bridge formation mold and (1 2') (2 1') a duplex bridge formation mold. This general formula (III) As an example of a transition-metals compound expressed (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-isopropylidene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (3-methyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (4, 5-benzoidenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4, 5-benzoidenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (4-isopropyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4-isopropyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (5, 6-dimethyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (5, 6-dimethyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-ethylene) screw (4, 7-diisopropyl indenyl) zirconium dichloride, - (2 (1 and 1'-ethylene) and 2'-ethylene) screw (4, 7-diisopropyl indenyl) Zirconium dichloride, (4-phenyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4-phenyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-ethylene) screw (3-methyl-4-isopropyl indenyl) zirconium dichloride, (3-methyl-4-isopropyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (5, 6-benzoidenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (5, 6-benzoidenyl) (1 and 1'-ethylene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-ethylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) (2 and 2'-methylene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-isopropylidene) (2 and 2'-isopropylidene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-propylidene) (2 and 2'-propylidene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-methylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-ethylene) (2 and 2'-isopropylidene)-screw (3-methylcyclopentadienyl) zirconium dichloride, - (2 (1 and 1'-methylene) and 2'-methylene) screw (3-methylcyclopentadienyl) zirconium dichloride (2 (1 and 1'-methylene) and 2'-ISO), A propylidene-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, - (2 (1 and 1'-ethylene) and 2'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1 and 1'-methylene) A (2 and 2'-methylene)-screw Zirconium dichloride, - (2 (1 and 1'-methylene) and 2'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-methylene) screw (3-methylcyclopentadienyl) zirconium dichloride, - (2 (1, 2'-ethylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride,

(3-methylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-isopropylidene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-ethylene) A (2 and 1'-methylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride, - (2 (1, 2'-methylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1, 2'-isopropylidene) What permuted zirconiums in these compounds, such as (2 and 1'-isopropylidene)-screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, by titanium or the hafnium can be mentioned. Of course, it is not limited to these.

[0033] The catalyst used for precuring in this invention as a transition-metals compound of the (A) component preferably Although at least two sorts chosen from the aforementioned (A-1) component (the BASF mold complex or the Hoechst mold complex), the component (A-2) (single bridge formation mold complex), and (A-3) the component (duplex bridge formation mold complex) are used Especially, the combination of a zirconium compound-hafnium compound, a zirconium compound-zirconium compound, and a hafnium compound-hafnium compound is suitable.

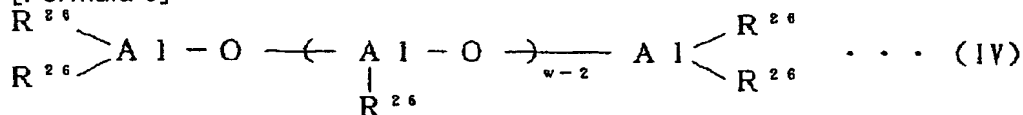
[0034] As an example with such suitable combination A single bridge formation mold zirconium complex-single bridge formation mold hafnium complex, a BASF mold zirconium complex-BASF mold hafnium complex, a Hoechst mold zirconium complex-Hoechst mold hafnium complex, a single bridge formation mold zirconium complex-BASF mold hafnium complex, A single bridge formation mold zirconium complex-Hoechst mold hafnium complex, a BASF mold zirconium complex-single bridge formation mold hafnium complex, a Hoechst mold zirconium complex-single bridge formation mold hafnium complex, the -two-fold BASF mold zirconium complex bridge formation mold hafnium complex, A -two-fold Hoechst mold zirconium complex bridge formation mold hafnium complex, -two-fold single bridge formation mold zirconium complex bridge formation mold hafnium complex, -two-fold duplex bridge formation mold zirconium complex bridge formation mold hafnium complex, and duplex bridge formation mold zirconium complex-BASF mold hafnium catalyst, A duplex bridge formation mold zirconium complex-Hoechst mold hafnium catalyst, a duplex bridge formation mold zirconium complex-single bridge formation mold hafnium complex, a single bridge formation mold zirconium complex-single bridge formation mold zirconium complex, a BASF mold zirconium complex-BASF mold zirconium complex, A Hoechst mold zirconium complex-Hoechst mold zirconium complex, a BASF mold zirconium complex-single bridge formation mold zirconium complex, a Hoechst mold zirconium complex-single bridge formation mold zirconium complex, the -two-fold BASF mold zirconium complex bridge formation mold zirconium complex, The -two-fold Hoechst mold zirconium complex bridge formation mold zirconium complex, a duplex bridge formation mold zirconium complex-single bridge formation mold zirconium complex, a -two-fold duplex bridge formation mold zirconium complex bridge formation mold zirconium complex, a single bridge formation mold hafnium complex-single bridge formation mold hafnium complex, A BASF mold hafnium complex-BASF mold hafnium complex, a Hoechst mold hafnium complex-Hoechst mold hafnium complex, a BASF mold hafnium complex-single bridge formation mold hafnium complex, a Hoechst mold hafnium complex-single bridge formation mold hafnium complex, The -two-fold BASF mold hafnium complex bridge formation mold hafnium complex, the -two-fold Hoechst mold hafnium complex bridge formation mold hafnium complex, a duplex bridge formation mold hafnium complex-single bridge formation mold hafnium complex, a -two-fold duplex bridge formation mold hafnium complex bridge formation mold hafnium complex, etc. are mentioned.

[0035] (A) the case where the combination of a zirconium compound and a hafnium compound is used as a transition-metals compound of a component -- the content of the zirconium compound in a mixed transition-metals compound -- desirable -- 1-99-mol % -- more -- desirable -- 2-95-mol % -- further -- desirable -- 5-90-mol % -- it is the 10-80-mol range of % especially preferably.

[0036] in the catalyst used for a precuring catalyst in this invention, it was chosen from the ionicity compound which reacts with an aluminum (B-1) oxy compound and said (B-2) transition-

metals compound, and can be changed into a cation as a (B) component and (B-3) clay, the clay mineral, and the ion-exchange nature stratified compound -- a kind is used at least. As an aluminum oxy compound of the above-mentioned (B-1) component, it is general formula (IV) [0037].

[Formula 9]



[0038] the inside of a formula, and R26 -- carbon numbers 1-20 -- desirable -- a hydrocarbon group or halogen atoms, such as an alkyl group of 1-12, an alkenyl radical, an aryl group, and an arylated alkyl radical, -- being shown -- w -- average degree of polymerization -- being shown -- usually -- 2-50 -- it is the integer of 2-40 preferably. in addition, every -- even if R26 is the same, it may differ. The chain-like aluminosilicate shown and general formula (V)

[0039]

[Formula 10]



[0040] (-- R26 and w are the same as the thing in said general formula (IV) among a formula.) -- the annular aluminosilicate shown can be mentioned. What is necessary is for there to be especially no definition about the means, and just to make it react according to a well-known approach, although the method of contacting alkylaluminum and condensing agents, such as water, is mentioned as a manufacturing method of said aluminosilicate. For example, there is an approach to which dissolve ** organoaluminum compound in the organic solvent, add the organoaluminum compound at the beginning at the time of the approach of contacting this in water, and ** polymerization, make trialkylaluminum react to the approach and ** tetra-ARUKIRUJI aluminosilicate to which the water of crystallization contained in the approach of adding water behind, ** metal salt, etc. and the water of adsorption to an inorganic substance or the organic substance are made to react with an organoaluminum compound, and water is made to react further. In addition, as aluminosilicate, you may be the thing of toluene insolubility.

[0041] One sort of these aluminum oxy compounds may be used, and they may be used combining two or more sorts. Although anything can be used if it is the ionic compound which reacts with said transition-metals compound and can be changed into a cation as a component (B-2) on the other hand General formula of the point of being able to form the polymerization active spot efficiently especially to a degree (VI) (VII) ([L1-R27] h+) a b ([Z]-) ... (VI) ([L2] h+) ... (VII) (however, L2 is M5, R28R29M6, R303 C, or R31M6.) a b ([Z]-) L1 among [(VI) and a formula (VII) Lewis base and [Z]- the anion to which two or more radicals combined non-ligating property anion [Z1] - with the element, i.e., [M4 G1 G2 ..., -- Gf] or here [[Z2]- and here] -- [Z1]- (here -- it is -- M4 -- the 5-15th group element of the periodic table -- the 13-15th group element of the periodic table is shown preferably.) G1 -Gf A hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-20, the dialkylamino radical of carbon numbers 2-40, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the aryloxy group of carbon numbers 6-20, the alkyl aryl radical of carbon numbers 7-40, the arylated alkyl radical of carbon numbers 7-40, the halogenation hydrocarbon group of carbon numbers 1-20, the acyloxy radical of carbon numbers 1-20, an organic metalloid radical, or the hetero atom content hydrocarbon group of carbon numbers 2-20 is shown, respectively. G1 -Gf Two or more may form the ring inside. f shows the integer of [(valence of the central metal M4) +1]. [Z2]- the logarithm of the inverse number of an acid dissociation constant (electric dissociation exponent) --ten or less Brønsted acid -- the conjugate base of the combination of independent or Brønsted acid, and Lewis acid or the conjugate base generally defined as super-strong acid is shown. Moreover, the Lewis base may configure. Moreover, R27 shows a hydrogen atom, the

alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, an alkyl aryl radical, or an arylated alkyl radical, and, as for a cyclopentadienyl group, a substituent cyclopentadienyl group, an indenyl group or a fluorenyl group, and R30, R28 and R29 show the alkyl group, the aryl group, alkyl aryl radical, or arylated alkyl radical of carbon numbers 1-20, respectively. R31 shows large annular ligands, such as a tetra-phenyl porphyrin and a phthalocyanine. In the ionic valence of [L1-R27] and [L2], h is the integer of 1-3 and a is one or more integers and b= (hxa). M5 The periodic table 1-3rds, 11-13, and 17 group element are included, and it is M6. The 7-12th group element of the periodic table is shown.] It can come out and what is expressed can be used suitably.

[0042] Here, it is L1. As an example Ammonia, monomethylamine, an aniline, dimethylamine, diethylamine, N-methylaniline, a diphenylamine, N,N-dimethylaniline, a trimethylamine, triethylamine, tree n butylamine, a methyl diphenylamine, a pyridine, p-BUROMO-N, N-dimethylaniline, p-nitro -Amines, such as N and N-dimethylaniline, Nitril, such as ester, such as thioether, such as phosphines, such as a triethyl phosphine, triphenyl phosphine, and diphenylphosphine, and tetrahydrothiophene, and ethyl benzoate, an acetonitrile, and a benzonitrile, can be mentioned.

[0043] As an example of R27, hydrogen, a methyl group, an ethyl group, benzyl, a trityl radical, etc. can be mentioned, and a cyclopentadienyl group, a methylcyclopentadienyl radical, an ethylcyclopentadienyl radical, a pentamethylcyclopentadienyl group, etc. can be mentioned as an example of R28 and R29. As an example of R30, a phenyl group, p-tolyl group, p-methoxyphenyl radical, etc. can be mentioned, and tetraphenylporphine, a phthalocyanine, an allyl compound, metallyl, etc. can be mentioned as an example of R31. M5 [moreover,] as an example -- Li, Na, K, Ag, Cu, Br, I, and I3 etc. -- it can mention -- M6 Mn, Fe, Co, nickel, Zn, etc. can be mentioned as an example.

[0044] (Moreover, [Z1]-, i.e., [M4 G1 G2, ... It sets to Gf] and is M4. As an example, B and aluminum are preferably mentioned for B, aluminum, Si, P, As, Sb, etc.) Moreover, G1 and G2 -Gf As an example As a dialkylamino radical, a dimethylamino radical, a diethylamino radical, etc., As an alkoxy group or an aryloxy group, a methoxy group, an ethoxy radical, an n-butoxy radical, a phenoxy group, etc., As a hydrocarbon group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, n-octyl radical, n-ray KOSHIRU radical, a phenyl group, p-tolyl group, benzyl, a 4-t-buthylphenyl radical, 3, 5-dimethylphenyl radical, etc., As a halogen atom, as a fluorine, chlorine, a bromine, iodine, and a hetero atom content hydrocarbon group p-fluoro phenyl group, 3, a 5-difluoro phenyl group, a pentachlorophenyl group, 3 and 4, 5-trifluoro phenyl group, a pentafluorophenyl radical, 3, 5-screw (trifluoromethyl) phenyl group, a screw (trimethylsilyl) methyl group, etc., A pentamethyl antimony radical, a trimethylsilyl radical, a trimethyl gel mill radical, a diphenyl arsine radical, a dicyclohexyl antimony radical, diphenyl boron, etc. are mentioned as an organic metalloid radical.

[0045] moreover It is the conjugate base of the combination of the Broensted acid independent not more than -10 or Broensted acid, and Lewis acid [Z2]. - As an example, the anion, i.e., electric dissociation exponent, of non-ligating property ** trifluoro methansulfonic acid anion () [CF3] SO3-, screw (trifluoromethane sulfonyl) methyl anion, screw (trifluoromethane sulfonyl) benzyl anion, screw (trifluoromethane sulfonyl) amide, and perchloric acid anion (ClO4) -, a trifluoroacetic acid anion () CF3 CO2-, a hexafluoro antimony anion () SbF6-, a fluorosulfonic acid anion () [FSO3] -, a chlorosulfonic-acid anion () [ClSO3] -, a fluorosulfonic acid anion / 5-antimony fluoride (FSO3 / SbF5) -, a fluorosulfonic acid anion / 5-fluoride arsenic (FSO3 / AsF5) -, trifluoro methansulfonic acid / 5-antimony fluoride () [CF3SO3] /SbF5- etc. -- it can mention.

[0046] As an example of such (B-2) a component compound Tetra-phenyl triethyl borate ammonium, tetra-phenyl boric acid tree n-butyl ammonium, tetra-phenyl boric acid trimethylammonium, tetra-phenyl boric acid tetraethylammonium, tetra-phenyl methyl borate (tree n-butyl) ammonium, Tetra-phenyl boric acid benzyl Ammonium, tetra-phenyl boric acid dimethyl diphenyl ammonium, tetra-phenyl boric acid triphenyl (methyl) ammonium, tetra-phenyl trimethyl borate anilinium, tetra-phenyl methyl borate pyridinium, (Tree n-butyl) Tetra-phenyl boric acid benzyl pyridinium, tetra-phenyl methyl borate (2-cyano pyridinium), Tetrakis Triethyl

borate ammonium, (Pentafluorophenyl) Tetrakis Boric acid tri-*n*-butyl ammonium, tetrakis (pentafluorophenyl) boric acid triphenyl ammonium, tetrakis (pentafluorophenyl) boric acid tetra-*n*-butyl ammonium, tetrakis (Pentafluorophenyl) Boric acid tetraethylammonium, tetrakis (pentafluorophenyl) boric acid benzyl (tri-*n*-butyl) ammonium, tetrakis (pentafluorophenyl) methyl borate diphenyl ammonium, tetrakis (Pentafluorophenyl) Boric acid triphenyl (Pentafluorophenyl) Ammonium, tetrakis (Methyl) Methyl borate anilinium, tetrakis (pentafluorophenyl) boric acid dimethyl anilinium, tetrakis (pentafluorophenyl) trimethyl borate anilinium, tetrakis (pentafluorophenyl) methyl borate pyridinium, (Pentafluorophenyl) Tetrakis (pentafluorophenyl) boric acid benzyl pyridinium, tetrakis (pentafluorophenyl) methyl borate (2-cyano pyridinium), Tetrakis (pentafluorophenyl) boric acid benzyl (2-cyano pyridinium), Tetrakis (Pentafluorophenyl) Methyl borate Tetrakis (4-cyano pyridinium) Boric acid triphenyl phosphonium, tetrakis [screw (3, 5-ditrifluoromethyl) phenyl] boric acid dimethyl anilinium, tetraphenyl boric acid ferro SENIUMU, tetra-phenyl boric acid silver, tetra-phenyl boric acid trityl, (Pentafluorophenyl) Tetra-phenyl boric acid tetra-phenyl porphyrin manganese, tetrakis (pentafluorophenyl) boric acid ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid (1 and 1'-dimethyl ferro SENIUMU), Tetrakis (pentafluorophenyl) boric acid decamethyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid silver, Tetrakis Boric acid trityl, tetrakis (Pentafluorophenyl) A boric acid lithium, tetrakis (Pentafluorophenyl) Sodium borate, tetrakis (Pentafluorophenyl) (Pentafluorophenyl) Boric acid tetra-phenyl porphyrin manganese, silver tetrafluoroborate, silver hexa-fluorophosphate, silver hexafluoroarsenate, silver perchlorate, silver tri-fluoroacetate, silver methanesulfonate, etc. can be mentioned.

[0047] One sort of ionicity compounds which are this (B-2) component and which react with the transition-metals compound of a ** (A) component, and can be changed into a cation may be used, and may be used combining two or more sorts. (B-3) As a component, clay, a clay mineral, or an ion-exchange nature stratified compound is used. Clay is the aggregate of a fine water silicate mineral, when a suitable quantity of water is mixed and kneaded, and plasticity is produced and it gets dry, rigidity is shown, and matter which will be sintered if it burns by high temperature is said. Moreover, a clay mineral means the water silicate which makes a clayey principal component. The field constituted by ionic bond etc. is the compound which takes the crystal structure piled up to parallel by the weak coupling force mutually, and an ion-exchange nature stratified compound means what has the exchangeable ion to contain. Most clay minerals are ion-exchange nature stratified compounds. Artificial composition of these may be carried out not only in a natural thing. As an ion-exchange nature stratified compound, the ion join character compound which has the **** structure of the shape of a layer, such as for example, a roppo maximum dense packing mold, an anti MOMON mold, a cadmium chloride mold, and a cadmium iodide mold, can be mentioned.

[0048] (B1 3) As an example of a component, a kaolin, a bentonite, kibushi clay, gairome clay, an allophane, a HISHINGERU stone, pyrophyllite, talc, a micaceous group, a montmorillonite group, a vermiculite, a chlorite group, a palygorskite, nacrite, dickite, halloysite, etc. are mentioned. (B-3) A thing 0.3-5ml [/g] or more has pore volume with a radius of 20A or more measured with the method of mercury penetration especially desirable as a component 0.1ml /or more. Moreover, it is also desirable to perform a chemical treatment from the impurity clearance in clay or structure, and the point of change of a function. Here, a chemical treatment puts both the surface treatment which removes the impurity which is acting to the front face as the ** person, and **** which affects the clayey crystal structure. Specifically, acid treatment, alkali treatment, salts processing, organic substance ****, etc. are mentioned. Acid treatment removes a surface impurity, and also increases surface area by making cations, such as aluminum in the crystal structure, iron, and magnesium, eluted. In alkali treatment, the clayey crystal structure is destroyed, moreover it brings about change of clayey structure, by salts processing and organic substance processing, ion complex, a molecular complex, organic complex, etc. can be formed, and surface area, the distance between layers, etc. can be changed. ion-exchange nature -- using -- the exchangeable ion of **** -- another ** -- also obtaining the matter between layers in the condition that between layers was expanded by permuting by high ion -- it is -- last ** It is also possible to still secure the polymerization reaction field in which a main catalyst

exists into between layers.

[0049] What could use the above-mentioned (B-3) component as it was, and could use what newly carried out addition adsorption of the water, or carried out **** dehydration ***** may be used. (B-3) As a component, a desirable thing is clay or a clay mineral, and the most desirable thing is a montmorillonite. (B1 3) As for a component, it is desirable to process with a silane system compound and/or an organoaluminium compound. Activity may improve by this processing. As this silane system compound, for example Trialkylsilyl chloride, such as trimethylsilyl chloride, triethyl silyl chloride, triisopropylsilyl chloride, tert-butyl dimethylsilyl chloride, tert-butylphenylsilyl chloride, and phenethyl dimethylsilyl chloride Dimethylsilyl dichloride, diethyl silyl dichloride, diisopropyl silyl dichloride, bis-diphenethyl silyl dichloride, methyl phenethyl silyl dichloride, diphenyl silyl dichloride, dimethylsilyl dichloride, Dialkyl silyl dichloride, such as JITORIRU silyl dichloride, methyl silyl trichloride, Alkyl silyl trichloride, such as ethyl silyl trichloride, isopropyl silyl trichloride, phenyl silyl trichloride, mesityl silyl trichloride, tolyl silyl trichloride, and phenethyl silyl trichloride And the halide which replaced the part of the above-mentioned chloride by other halogens A screw An amine, a screw (Trimethylsilyl) An amine, a screw (Triethyl silyl) An amine, a screw (dimethyl ethyl silyl) amine, a screw (diethyl methyl silyl) amine, a screw (dimethylphenyl silyl) amine, a screw (dimethyl tolyl silyl) amine, a screw (dimethyl mesityl silyl) amine, (Triisopropyl silyl) Silylamine, such as N and N 1 dimethylamino trimethyl silane, a trimethyl (diethylamino) silane, and N-(trimethylsilyl) imidazole The poly silanols called by the trivial name of par alkyl polysiloxy polyol Silanols, such as a tris (trimethylsiloxy) silanol Silylamide **, such as N, O-screw (trimethylsilyl) acetamide, a screw (trimethylsilyl) trifluoro acetamide, N-(trimethylsilyl) acetamide, a screw (trimethylsilyl) urea, and a trimethylsilyl diphenylurea, Cyclosiloxanes, such as straight chain-like siloxanes, such as 1 and 3-dichloro tetramethyl disiloxane, and a pentamethyl cyclopentane siloxane Tetraalkylsilanes, such as a dimethyl diphenyl silane, a diethyl diphenyl silane, and a diisopropyl diphenyl silane A trimethyl silane, a triethyl silane, a triisopropyl silane, Trialkyl silanes, such as a tree t 1 butyl silane, a triphenyl silane, a tritoyl silane, a TORIMESHI chill silane, a methyl diphenyl silane, dinaphthyl methylsilane, and screw (diphenyl) methylsilane Inorganic silicon compounds, such as tetrachlorosilane and silicon tetrabromide, are mentioned. It is silylamine preferably among these and is trialkyl silane chloride more preferably. Although one kind of silane system compound may be used from the inside of these, it is also possible to use for arbitration combining two or more kinds depending on the case.

[0050] Furthermore, although there is especially no limit as an organoaluminium compound used for processing of a component (B-3), the meeting object of the annular aluminosilane or annular aluminosilane expressed with the straight chain-like aluminosilane or the above-mentioned general formula (V) expressed with the alkyl group content aluminium compound expressed with the general formula (VIII) mentioned later and the same formula, for example and the above-mentioned general formula (IV) can be used preferably. In seashell body, trialkylaluminums, such as trimethylaluminum, triethylaluminum, TORIPURO pill aluminum, triisobutylaluminum, and tree t-butyl aluminum, Halogens, such as dimethyl aluminum chloride, diethyl ARUMIUMU chloride, a dimethyl aluminum methoxide, a diethyl aluminum methoxide, dimethyl aluminum hydroxide, and diethyl aluminum hydroxide, an alkoxy group Or the alkylaluminum of hydrogen atom content, such as alkylaluminum of hydroxyl-group content, a dimethyl aluminum hydride, and a diisobutyl aluminum hydride, It is aluminosilane, such as methyl aluminosilane, ethyl aluminosilane, and isobutyl aluminosilane, etc., and especially trimethylaluminum or triisobutylaluminum is [among these] desirable. (B-3) One sort of organoaluminium compounds used for processing of a component may be used from the inside of these, and may be used combining two or more sorts.

[0051] (B-3) Although there is no limit in ** about the operating rate of the silane system compound and organoaluminium compound which are used for processing of a component, when a component (B1 3) is clay or a clay mineral It is the rate that 0.1-100000 mols of silicon original hands in a silane system compound usually become 0.5-10000 mols preferably to one mol of hydroxyl groups in a component. (B-3) Moreover, when using organic aluminum-ized ****, 0.1-100000 mols of aluminum atoms in an organoaluminium compound are usually used at a rate which becomes 0.5-10000 mols preferably. Moreover, it is the rate that the silicon atom in a

silane system compound is set to 0.001-100g to 1g (B-3) of components when a component (B-3) is except clay or a clay mineral, and when using an organoaluminium compound, it uses at a rate that the aluminum atom in an organoaluminium compound is set to 0.001-100g, and things are desirable. If out of range, there is a thing which is the above-mentioned rate and which polymerization activity falls. (B-3) Processing of a component may be performed in inert gas, such as nitrogen, or hydrocarbons, such as a pentane, a hexane, toluene, and a xylene. Furthermore, it is desirable to carry out between the boiling points of a room temperature to an activity solvent especially during the boiling point of an activity solvent from -30 degrees C as well as the ability to perform this processing under polymerization temperature.

[0052] In the polymerization catalyst in this invention, as this (B) component, a component (B-1), a component (B-2), and a component (B-3) may be used independently, and you may use combining these. the case where a compound is used for the operating rate of (A) catalyst component and (B) catalyst component in this precuring catalyst as a (B) catalyst component (B-1) -- a mole ratio -- desirable -- 1:1-1:106 -- more -- desirable -- 1:10-1:104 The range is desirable, and when deviating from the above-mentioned range, the catalyst cost per unit weight polymer becomes high, and is not practical. (B-2) the case where a compound is used -- a mole ratio -- desirable -- 10:1-1:100 -- the range of 2:1-1:10 is more preferably desirable. When deviating from this range, the catalyst cost per unit weight polymer becomes high, and it is not practical. moreover, the case where clay or a clay mineral is used as a compound (B-3) -- the mole ratio of the hydroxyl group in (A) catalyst component and (B) catalyst component -- desirable -- 1:0.1-1:100000 -- the range of 1:0.5-1:10000 is more preferably desirable. Furthermore, when an ion-exchange nature stratified compound is used as a compound (B-3), the operating rates of (A) catalyst component and (B) catalyst component are 1:1-1:100000 preferably in a weight ratio. When deviating from this range, the catalyst cost per unit weight polymer becomes high, and it is not practical.

[0053] Furthermore, the catalyst used for precuring in this invention may contain the aforementioned (A) component and the (B) component as a principal component, and is (A). The (C) organoaluminium compound and/or support may be contained as a principal component in a component and (B) component list. As for this support, it is desirable to use it, when a catalyst is what does not contain a component as a (B) component (B-3).

[0054] Here, as an organoaluminium compound of the (C) component, it is general formula (VIII) $R_{32}vAlQ_3-v$. The compound shown by ... (VIII) (R_{32} shows the alkyl group of carbon numbers 1-10 among a formula, Q shows a hydrogen atom, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, or a halogen atom, and v is the integer of 1-3) is used. Said general formula (VIII) As an example of the compound shown, trimethylaluminum, triethylaluminum, triisopropyl aluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminium chloride, methyl aluminum dichloride, ethyl aluminum dichloride, a dimethyl aluminum fluoride, a diisobutyl aluminum hydride, a diethyl aluminum hydride, ethylaluminium sesquichloride, etc. are mentioned. Preferably, they are trimethylaluminum, triethylaluminum, and triisobutylaluminum. One sort of these organoaluminium compounds may be used and they may be used combining two or more sorts. moreover, the operating rate of (A) catalyst component and the (C) organoaluminium compound used by request -- a mole ratio -- desirable -- 1:1-1:20000 -- more -- desirable -- 1:5-1:2000 -- the range of 1:10-1:1000 is still more preferably desirable. Although the polymerization activity per 1g of transition-metals compounds can be raised by using an organoaluminium compound, while an organoaluminium compound becomes useless when, and deviating especially from the above-mentioned range, it may remain so much in a polymer, and when few, sufficient catalytic activity may not be acquired, and it may not be desirable. [too much]

[0055] In this invention, even if there are few each catalyst components, a kind can be supported and used for suitable support. (C) Although there is especially no limit about the class of support of a component and both inorganic oxide support the other inorganic support and organic support can be used, the inorganic oxide support from a point or the other inorganic support of mol HOROJI-control is especially desirable. Specifically as inorganic oxide support, it is SiO₂, aluminum 2O₃, MgO, ZrO₂, TiO₂, Fe 2O₃, B-2 O₃, and CaO, ZnO, BaO and ThO₂. Such

mixture, for example, a silica alumina, a zeolite, a ferrite, glass fiber, etc. are mentioned. Especially in these, it is SiO_2 . Or aluminum 2O_3 It is desirable. In addition, the above-mentioned inorganic oxide support may contain a small amount of carbonate, a nitrate, a sulfate, etc. [0056] on the other hand -- as support other than the above -- MgCl_2 and $\text{Mg}(\text{OC two H}_5)_2$ etc. -- general formula $\text{MgR}_{33}\text{X X7 y}$ represented with a magnesium compound etc. The magnesium compound expressed, its complex salt, etc. can be mentioned. Here, R33 is the alkyl group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20 or the aryl group of carbon numbers 6-20, and X7. The alkyl group of a halogen atom or carbon numbers 1-20 is shown, 0-2y are 0-2, and x is $x+y=2$. every -- R33 and every -- X7 respectively -- being the same -- moreover, it may differ or you may be. Moreover, as organic support, polymers, such as a polystyrene and styrene-divinylbenzene copolymer, polyethylene, polypropylene, permutation polystyrene, and polyarylate, starch, carbon, etc. can be mentioned. as the support used in this invention -- MgCl_2 , $\text{MgCl}(\text{OC two H}_5)$, $\text{Mg}(\text{OC two H}_5)_2$, SiO_2 , and aluminum 2O_3 etc. -- it is desirable. Moreover, although the description of support changes with the classes and processes, 10-200 micrometers of mean particle diameter are 1-300 micrometers usually 20-100 micrometers more preferably. If particle size is small, the fines in a polymer will increase, and if particle size is large, the big and rough particle in a polymer will increase, and it will become lowering of bulk density, and the cause of plugging of a hopper. moreover, the specific surface area of support -- usually -- $1-1000\text{m}^2 / \text{g}$ -- desirable -- $50-500\text{m}^2 / \text{g}$, and pore volume -- usually -- $0.1-5\text{cm}^3 / \text{g}$ -- they are $0.3-3\text{cm}^3 / \text{g}$ preferably.

[0057] When either specific surface area or pore volume deviates from the above-mentioned range, catalytic activity may fall. In addition, it can ask for specific surface area and pore volume from the volume of the nitrogen gas with which it adsorbed according to the BET adsorption method (J. refer to Am.Chem.Soc, the 60th volume, and the 309th page (1983)). Furthermore, as for the above-mentioned support, it is usually desirable to calcinate and use at 200-800 degrees C preferably 150-1000 degrees C. When [of a catalyst component] making said support support a kind at least, it is desirable from points, such as applicability to processes, such as MORUHO logy control and a vapor phase polymerization, to make both (A) catalyst component and (B) catalyst component support preferably either [at least] (A) catalyst component or (B) catalyst component.

[0058] About the approach of making this support supporting either [at least] the (A) component or the (B) component How to mix at least one side and support of ** (A) component and the (B) component, for example, although not restricted especially, ** After processing support with an organoaluminium compound or a halogen content silicon compound, How to mix with either [at least] the (A) component or the (B) component in an inert solvent, ** The approach to which support, the (A) component, the (B) component, its both and organoaluminium compound, or a halogen content silicon compound is made to react, ** Face the catalytic reaction of the approach of mixing with the (B) component or the (A) component, the approach of mixing the catalytic-reaction object of ** (A) component and the (B) component with support, ** (A) component, and the (B) component after making support support the (A) component or the (B) component. The approach of making support living together etc. can be used. In addition, the organoaluminium compound of the (C) component can also be added in the reaction of the above-mentioned **, **, and **.

[0059] Thus, after the acquired catalyst once performs solvent distilling off and takes it out as a solid-state, it may be used for precuring, and it may be used for precuring as it is. In this invention, 10^{-6} to ten - two mols of (A) components are usually preferably used per 1g of support in the amount of 3×10^{-6} to ten - three mols. Moreover, the operating rate of the (B) component [(B-1) a component, a component (B-2), and a component (B-3)] to the (A) component is as above-mentioned.

[0060] When the operating rate of a ** (B) component [(B-1) a component, a component (B-2), and a component (B-3)] and support or the operating rate of the (A) component and support deviates from the above-mentioned range, activity may fall. thus, the mean particle diameter of the prepared catalyst -- usually -- 2-500 micrometers -- desirable -- 10-400 micrometers -- especially -- desirable -- 20-200 micrometers -- it is -- specific surface area -- usually -- 20-

1000m² / g -- it is 50-500m²/g preferably. When mean particle diameter is less than 2 micrometers, the fines in a polymer may increase, and when it exceeds 500 micrometers, the big and rough particle in a polymer may increase. When specific surface area is under 20m² / g, activity may fall, and when 1000m² / g is exceeded, the bulk density of a polymer may fall. Thus, advantageous high bulk density and the polyolefine which has the outstanding particle size distribution can be industrially obtained by supporting to support.

[0061] The precuring catalyst of this invention is first manufactured under existence of said catalyst by [which carry out the polymerization of a kind at least] having been chosen out of the alpha olefin and annular olefin of carbon numbers 2-20. Here as an alpha olefin of carbon numbers 2-20 Ethylene, a propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, etc. are mentioned. As an annular olefin Cyclopentene, a cyclo heptene, norbornene, 5-ethyl-2-norbornene, tetracyclo dodecen, etc. are mentioned. As a polymerization format, you may be any of a batch process and continuous system, and the approach of arbitration can be adopted out of a slurry polymerization method, a vapor-phase-polymerization method, a bulk-polymerization method, a solution polymerization method, etc.

[0062] As a polymerization solvent used when carrying out a slurry polymerization or solution polymerization, halogenated hydrocarbon, such as aromatic hydrocarbon, such as alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Deccan, a dodecane, and kerosene, a cyclopentane, a cyclohexane, and a methylcyclohexane, benzene, toluene, and a xylene, ethylene chloride, a chlorobenzene, dichloromethane, and chloroform, etc. is mentioned, for example. These solvents may be used independently, and two or more sorts may be mixed and used. About polymerization conditions, the range of -20-150 degrees C of polymerization temperature is -50-200 degrees C usually 0-120 degrees C more preferably. the polymerization preassure force -- usually -- 0-200 kg/cm² G -- desirable -- 0.1-150 kg/cm² G -- 0.2-100kg/cm² is the range of G more preferably. moreover, polymerization time amount -- usually -- it is the range of 1 minute - 10 hours more preferably for 30 seconds to 30 hours for 10 seconds to 40 hours. furthermore, the amount of the catalyst used -- a raw material monomer / (aforementioned A) component mole ratio -- desirable -- 1-108 -- more -- desirable -- 100-107 Choosing so that it may become is advantageous.

[0063] Moreover, a polymerization catalyst can be made to generate in this invention by performing support actuation to one [at least] support of the (A) component and the (B) component within a polymerization system. For example, said organoaluminium compound is further added as occasion demands with the (A) component and the (B) component, and support, and it is an olefin 0.1-50kg/cm² In addition, the approach of performing precuring at -20-200 degrees C for 1 minute to about 40 hours, and making a catalyst particle generating can be used. The control (control of molecular weight) of the limiting viscosity of polyolefine made into the precuring catalyst generated by precuring or the object is said within the limits, and can perform the operating rate of each component of a polymerization catalyst, the amount of the polymerization catalyst used, polymerization temperature, the polymerization preassure force, etc. by selecting suitably.

[0064] The precuring catalyst acquired by such precuring is a per [in the range whose limiting viscosity [eta] is 0.1-20 deciliters/g / 1g of transition-metals compounds / 0.01-2000g] thing. Limiting viscosity [eta] is measured in the temperature of 135 degrees C among a tetralin solvent. While this limiting viscosity [eta] is inferior to melting workability in a polymerization or the polyolefine obtained by copolymerizing about an alpha olefin etc. ing, using this precuring catalyst in less than 0.01 deciliters /, if a mechanical strength is inadequate and g is exceeded in 20 deciliters /, the melt viscosity of the above-mentioned polyolefine will be high, and melting workability will fall. From fields, such as the melting workability of the above-mentioned polyolefine, and balance of a mechanical strength, as this limiting viscosity [eta], g is desirable in 0.05-20 deciliters /, and the range which is 0.1-18 deciliters/g is especially desirable.

[0065] Although the precuring catalysts acquired by precuring are per [0.01-2000g] 1g of transition-metals compounds of the (A) component, per [0.1-150g] 1g of transition-metals

compounds are desirable, and they are desirable. [of 1-especially 120g]

[0066] The precuring catalyst manufactured by the above-mentioned precuring is a thing in the condition that the polymer adhered to the perimeter of a catalytic activity component, and this polymer and the catalyst are included in the reaction mixture after precuring termination. In this invention, this polymer and a catalyst (catalyst to which this polymer adhered when putting in another way) are called a precuring catalyst. the manufacture approach of this invention -- setting -- the bottom of existence of this precuring catalyst -- or it was chosen as the bottom of existence out of the alpha olefin, annular olefin, and styrene monomer of carbon numbers 2-20 although the organoaluminium compound was added as occasion demands -- polyolefine can be obtained for a kind a polymerization or by copolymerizing at least. Here, the same thing as the above can be used as an organoaluminium compound. (A) the case where the operating rate of a catalyst component and the organoaluminium compound used by request is that in which said precuring catalyst does not contain an organoaluminium compound -- a mole ratio -- desirable -- 1:1-1:20000 -- more -- desirable -- 1:5-1:2000 -- the range of 1:10-1:1000 is still more preferably desirable. Moreover, although it changes with the amount used when said precuring catalyst is a thing containing an organoaluminium compound The mole ratio of the transition-metals compound in a precuring catalyst, and an organoaluminium compound, not using an organoaluminium compound at all 1:0.5-1:10000 and by using an organoaluminium compound in 1:2-1:8000 more preferably Although the polymerization activity per transition metals can be raised, while an organoaluminium compound becomes useless when, and deviating especially from the above-mentioned range, it may remain so much in a polymer, and when few, sufficient catalytic activity may not be acquired, and it may not be desirable. [not much]

[0067] The thing same as the alpha olefin of carbon numbers 2-20 and an annular olefin as the above is mentioned. moreover, as a styrene monomer Styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, 2, 4-dimethyl styrene, 2, 5-dimethyl styrene, 3, 4-dimethyl styrene, 3, 5-dimethyl styrene, 2 and 4, 5-trimethyl styrene, 2 and 4, 6-trimethyl styrene, Alkyl styrene, such as p-t-butyl styrene, p-chloro styrene, m-chloro styrene, o-chloro styrene, Halogenation styrene, such as p-bromostyrene, m-bromostyrene, o-bromostyrene, p-fluoro styrene, m-fluoro styrene, o-fluoro styrene, and o-methyl-p-fluoro styrene, etc. is mentioned.

[0068] A polymerization format and polymerization conditions can be made into the same thing as said precuring. moreover -- a block -- a pile -- the block copolymer of an olefin can also be lawfully manufactured more by different reaction condition from precuring. In this case, a different reaction condition is the following reaction step, after manufacturing the homopolymer of polypropylene first for example, using ** precuring catalyst. It is made to be the same as that of copolymerizing the monomer chosen from ethylene, the alpha olefin of carbon numbers 4-20, an annular olefin, and styrene, and a propylene, or the ** above-mentioned **. After copolymerizing the monomer and propylene which were chosen from ethylene, the alpha olefin of carbon numbers 4-20, an annular olefin, and styrene, It is manufacturing the block copolymer from which the preparation presentation of a monomer was changed at the following step, and the copolymerization presentation changed etc., and a monomer kind, polymerization temperature, a pressure, time amount, and a monomer brewing presentation are changed, and it points out performing a polymerization reaction in two or more steps.

[0069] The range of 50 degrees C or more of 60 degrees C or more of 70 degrees C or more of melting points of the polyolefine obtained by the approach of this invention is usually 80-160 degrees C still more preferably more preferably. In addition, this melting point is the value measured by the following approach. That is, after carrying out temperature up from a room temperature to 200 degrees C the rate for 10-degree-C/and holding for 3 minutes at 200 degrees C using a differential scanning calorimeter [the product made from SEIKO Electronic industry, and DSC200 mold], the temperature is lowered to 30 degrees C by part for 10-degree-C/. Carry out temperature up by part for 10-degree-C/, and let temperature of the fusion peak which appears in that case be the melting point, after holding for 5 minutes at 30 degrees C. As for this polyolefine, what has a melt index MI in the range for 0.005-1000g / 10 minutes is desirable. This MI has an inadequate melting fluidity in 0.005g / less than 10 minutes, and if it exceeds 1000g / 10 minutes, machine physical properties fall remarkably and are not desirable.

From fields, such as balance of a melting fluidity and machine physical properties, more desirable MI is the range for 0.01-800g / 10 minutes, and its range for 0.05-600g / 10 minutes is especially desirable. In addition, this MI is ASTM. It is the value measured on the temperature of 230 degrees C, and the conditions of 2.16kg of loads based on D1238-T65.

[0070] For the melting tension MS of the above-mentioned polyolefine (g), the limiting viscosity [eta] (deciliter/g) measured in the temperature of 135 degrees C among the melting tension MS (g) measured in the temperature of 230 degrees C and a tetralin solvent is a formula.

$$\log MS \geq 3.17 \times \log [\eta] - 0.68 \quad (1)$$

It is desirable to fill *****. When logMS is smaller than the value of "3.17xlog[eta]-0.68", it is inferior to melting workability and the object of this invention is not reached. from the field of melting workability -- further -- desirable -- $\log MS \geq 3.17 \times \log [\eta] - 0.57$ -- desirable -- $\log MS \geq 3.17 \times \log [\eta] - 0.46$ -- it is $\log MS \geq 3.17 \times \log [\eta] - 0.35$ especially preferably. The melting tension MS is the value measured on condition that the following using the KYAPI log rough by the Oriental energy machine company.

a part for capillary tube : 3.14m/-- Temperature : [] -- in addition, 4000 weight ppm addition of the 230 degrees C of the mixture of the weight ratio 1:1 of IRUGA NOx 1010 and BHT was beforehand carried out as an antioxidant at the measurement sample. : The diameter of 2.095mm, die length of 8.0mm, and 90 fluid inlet angles Diameter of a cylinder : 9.0mm Cylinder extrusion rate : A part for 10mm/ Rolling-up rate

[0071] The bulk density of the above-mentioned polyolefine has desirable cc in 0.2-0.5g /, and its cc is especially desirable in 0.3-0.5g /. In addition, bulk density is JIS. It asked based on K6721.

[0072]

[Example] Next, although an example explains this invention in more detail, this invention is not limited at all by these examples.

Preparation SiO227.1(Fuji SHIRISHIA chemistry company make, trade name---10) g of n-heptane suspension of example of preparation 1 silica support methyl aluminoxane was heat-treated under the 2-hour nitrogen air current at 200 degrees C, and desiccation silica 25.9g was obtained. It was dropped with the dropping funnel, having covered 145.5ml of 1.5 mols [/l.] methyl aluminoxane toluene solutions over this for 1.0 hours, having supplied this desiccation silica in 400ml of toluene cooled at -78 degrees C, and stirring it by dry ice / methanol bath.

After leaving it in this condition for 4.0 hours, temperature up was carried out from -78 degrees C to 20 degrees C in 6.0 hours, and it was further left in this condition for 4.0 hours. Then, the reaction of a silica and methyl aluminoxane was made to complete by carrying out temperature up from 20 degrees C to 80 degrees C in 1.0 hours, and leaving it at 80 degrees C for 4.0 hours.

[0073] At 60 degrees C, twice, filtered this suspension at 60 degrees C, the obtained solid was carried out at 60 more degrees C by 400ml toluene, and washing was carried out by 400ml n-hexane. By carrying out reduced-pressure-drying processing of the solid after washing at 60 degrees C for 4.0 hours, silica support methyl aluminoxane 33.69g was obtained. The amount of support of methyl aluminoxane was 23.12 % of the weight. Thus, n-heptane was added to the obtained silica support methyl aluminoxane whole quantity, full capacity was made into 500ml, and suspension with a methyl aluminoxane concentration of 0.27 mols [/l.] was prepared.

[0074] 9.26ml (methyl aluminoxane 2.5 millimol) of silica support methyl aluminoxane suspension obtained in the example 1 of preparation preparation of an example of preparation 2 silica support metallocene catalyst was extracted in the desiccation nitrogen-purge container, and 20ml of n-heptanes was added and stirred. To this suspension, as a transition-metals compound, toluene solution 5 micromole of rac-dimethylsilane diyl-bis--1-(2-methyl-4-phenyl indenyl) zirconium dichloride [rac-Me2 Si(2-Me-4-PhInd)2 ZrCl2], Toluene solution 5 micromole of rac-dimethylsilane diyl-bis--1-(2-methyl-4-phenyl indenyl) hafnium dichloride [rac-Me2 Si(2-Me-4-PhInd)2 HfCl2] was added, and it stirred at the room temperature for 0.5 hours. Then, the solid-state catalyst component which stopped stirring, and the solid-state catalyst component was made to sediment, and sedimented is light yellow, and it checked that a solution was transparent and colorless. Thus, the silica support metallocene catalyst was prepared.

[0075] After it heated the proof-pressure autoclave made from 1.4l. stainless steel with

manufacture stirring equipment of an example 1 polypropylene system precuring catalyst at 80 degrees C and it fully carried out reduced pressure drying, it returned to the atmospheric pressure with desiccation nitrogen, 400ml [of desiccation deoxidation n-heptanes] and triisobutylaluminum (toluene solution) 0.5 millimol was supplied to this autoclave under the desiccation nitrogen air current, and it stirred for 10 minutes by 500rpm. The silica support metallocene catalyst prepared in the example 2 of preparation was thrown into this (they are ten micromole by the sum total of a zirconium compound and a hafnium compound), 8.0kg/cm² of propylenes was continuously supplied by G, controlling at 30 degrees C, precuring was carried out for 90 minutes, and polypropylene (precuring catalyst) was obtained. Depressuring of the unreacted propylene was carried out after precuring termination, and nitrogen removed the unreacted propylene further. When some obtained polypropylene was sampled under nitrogen-gas-atmosphere mind and the amount of precuring (the amount of polypropylene obtained by precuring) was calculated, it was 2620g per 1g of transition metals, and was 27.9g per 1g of silica support metallocene catalysts. Moreover, the limiting viscosity [eta] of the polypropylene obtained by precuring was 3.3 deciliters/g. The precuring catalyst acquired by precuring separated the solid-state part from the liquid part by the decantation, and saved it as a slurry of 100ml of desiccation deoxidation n-heptanes.

[0076] After it heated the proof-pressure autoclave made from 1.4l. stainless steel with manufacture stirring equipment of the polypropylene using an example 2 precuring catalyst at 80 degrees C and it fully carried out reduced pressure drying, it returned to the atmospheric pressure with desiccation nitrogen, 300ml [of desiccation deoxidation n-heptanes] and triisobutylaluminum (toluene solution) 0.5 millimol was supplied to this autoclave under the desiccation nitrogen air current, and it stirred for 10 minutes by 500rpm. 100ml (it is an equivalent for nine micromole by the zirconium and hafnium atom conversion) of precuring catalysts prepared in the example 1 was supplied to this, and temperature up was carried out to it to 70 degrees C. 8.0kg/cm² of propylenes was continuously supplied to this by G, and the polymerization was carried out for 30 minutes. Depressuring of the unreacted propylene was carried out after reaction termination, with the methanol of a large quantity, it deactivated, filtration desiccation processing of the catalyst was carried out, and polypropylene 189g was obtained. About this polypropylene, a melt index MI, limiting viscosity [eta], the melting tension MS, the melting point Tm, and bulk density were asked for and evaluated according to the approach indicated in the description text. A result is shown in the 1st table.

[0077] In the manufacture example 1 of an example 3 polyethylene system precuring catalyst, the propylene was changed into ethylene and polyethylene (precuring catalyst) was manufactured like the example 1 except having set polymerization time amount as for 45 minutes. When some obtained polyethylene was sampled under nitrogen-gas-atmosphere mind and the amount of precuring (the amount of polyethylene obtained by precuring) was calculated, it was 2740g per 1g of transition metals, and was 29.3g per 1g of silica support metallocene catalysts. Moreover, the limiting viscosity [eta] of the polyethylene obtained by precuring was 3.3 deciliters/g. The precuring catalyst acquired by precuring separated the solid-state part from the liquid part by the decantation, and saved it as a slurry of 100ml of desiccation deoxidation n-heptanes.

[0078] 184g of ethylene propylene rubbers was manufactured like the example 2 except having used what was prepared in the example 3 as manufacture precuring intermediation of the ethylene propylene rubber using an example 4 precuring polymerization catalyst.

[0079]

[A table 1]

第 1 表

	実施例 2	実施例 4
収量 (g)	1 8 9	1 8 4
M I (g/10分)	0. 3 5	0. 4 3
極限粘度 [η] (dl/g)	2. 4 9	2. 5 9
融点 (°C)	1 4 7. 8	1 4 8. 0
嵩密度 (g/cc)	0. 4 5	0. 4 0
熔融張力 (g)	9. 0	6. 9

[0080]

[Effect of the Invention] According to this invention, melting tension is high, it excels in resin phase solubility, and the high polyolefine of bulk density can be manufactured cheaply and efficiently.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] About the manufacture approach of polyolefine, in more detail, melting tension of this invention is high, it is excellent in resin phase solubility, and relates to the approach of manufacturing the high polyolefine of bulk density cheaply and efficiently.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Polyolefine is broadly used in many fields taking advantage of the outstanding property. However, in the conventional polyolefine, melting tension and melting viscoelasticity ran short, the phenomenon of drawdown tended to happen to **** inferior to the stability of the parison in large-sized blow molding, and shaping of large-sized components was difficult. Moreover, in order to raise melting tension, when macromolecule quantification is carried out, a melting fluidity falls and the problem of being inapplicable to shaping of a complicated configuration arises.

[0003] Moreover, in the field of a foaming object, although the demand to the foaming object which has thermal resistance with lightweight-izing, adiathermic, damping nature, etc. increases and the polypropylene nature foaming object is expected, what the foaming object melting tension is insufficient and it may fully be satisfied with conventional polypropylene of an object is hard to be acquired from is the actual condition. In order to make the field of the invention of this polypropylene expand further, extrusion-molding workability needs to be improved. The approach of improving melting workability, the method of making polyolefine construct a bridge selectively and improving melting workability, etc. are tried by making variously the attempt which is going to improve the melting workability of polyolefine, for example, improving the polymerization catalyst and polymerization formula at the time of manufacture of polyolefine, and expanding the molecular weight distribution conventionally.

[0004] On the other hand, in the ethylene system polymer, although a molecular weight distribution is narrow, the ethylene system polymer with which melting tension was improved is proposed by the catalyst system which combined a metallocene catalyst, aluminoxane, etc. recently (JP,4-213306,A). Moreover, also about the ethylene system polymer manufactured according to a restricted geometry mold catalyst, although molecular weight distribution are narrow similarly, it is indicated that melting tension is improved (JP,3-163088,A) and existence of long-chain branching is suggested. However, the improvement in extrusion-molding workability is still small by the improvement in melting tension. Moreover, although melting tension is [resin / polystyrene system / polyethylene system resin or a polypropylene resin] high, in the sheet forming of deep drawing etc., it is still deficient in performance.

[0005] Although a melting working characteristic will generally improve by the branching if long-chain branching is introduced into a polymer chain, it is the so-called composite-material field which consists of a different-species polymer in the branched polymer which constituted branched chain from a different monomer from a principal chain polymer, and it is possible to reduce the boundary tension between different-species polymers, to raise the dispersibility of a polymer, and to give effectively physical properties which can be easily incompatible, such as impact strength and rigidity. Moreover, since micro phase separation structure is taken, the application to various elastomers is also possible. However, since introducing branching had a limit in the polyolefine field until now, there was a limitation of application expansion. If this becomes possible, the application field is expected to expand greatly from the outstanding machine physical properties which polyolefine originally has, and the environmental compatibility represented by recycle nature.

[0006] by the way, as an approach of improving the melting tension of polyolefine and raising a

melting working characteristic How to mix the high density polyethylene of the amount of giant molecules with high (1) melting tension until now (JP,6-55868,B), (2) How to mix high density polyethylene with the high melting tension manufactured according to a chromium system catalyst (JP,8-92438,A), (3) How to mix the low density polyethylene manufactured by the general high voltage radical polymerization method, (4) How to raise melting tension to common polyolefine by carrying out an optical exposure, (5) How to raise melting tension to common polyolefine by carrying out an optical exposure under existence of a cross linking agent and a peroxide, (6) The approach of carrying out the graft of the radical polymerization nature monomers, such as styrene, to common polyolefine, the approach (JP,5-194778,A, JP,5-194779,A) of carrying out copolymerization of (7) olefins and the polyene, etc. are tried. [0007] However, in the approach of aforementioned (1) - (3), since the elastic modulus of the component which heightens melting tension, reinforcement, and thermal resistance run short, it does not escape polyolefine and that the description of polypropylene original especially is spoiled. Moreover, in the above (4) and the approach of (5), when it is difficult to control the crosslinking reaction which occurs as side reaction and an adverse effect arises in a poor appearance and a mechanical characteristic according to generating of gel, a limitation is to control fabricating-operation nature to arbitration, and there is a problem that a control range is narrow. Furthermore, in the approach of the above (6), a problem is produced in generating and the manufacturing cost of gel, and in the approach of the above (7), the amelioration effectiveness of melting tension is small, and when sufficient effectiveness is not demonstrated, we are anxious also about generating of gel.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, melting tension is high, it excels in resin phase solubility, and the high polyolefine of bulk density can be manufactured cheaply and efficiently.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Under such a situation, melting tension of this invention is high, it is excellent in resin phase solubility, and aims at offering the approach of manufacturing the high polyolefine of bulk density cheaply and efficiently.

[0009] this invention persons found out melting tension being high a polymerization or by copolymerizing, excelling an alpha olefin, an annular olefin, or a styrene monomer in resin phase solubility, and the polyolefine which has properties, like bulk density is high being obtained, and attaining the object under existence of the precuring catalyst which is made to carry out precuring of the olefin to the bottom of existence of a specific catalyst, and is acquired, as a result of repeating research wholeheartedly, in order to attain the above-mentioned object. This invention is completed based on this knowledge.

[0010] Namely, at least two sorts as which this invention was chosen from the transition-metals compounds of the 4th group of the periodic table who has the (A) cyclopentadienyl group, (B) (B-1) Under existence of the catalyst which was chosen as the ionicity compound list which reacts with an aluminum oxy compound and the above-mentioned (B-2) transition-metals compound, and can be changed into a cation from clay (B-3), the clay mineral, and the ion-exchange nature stratified compound and which comes to contain a kind at least, it was chosen out of the alpha olefin and annular olefin of carbon numbers 2-20 -- at least a kind The precuring catalyst characterized by coming to carry out a polymerization at a per [1g of above-mentioned transition-metals compounds / 0.01-2000g] rate, and being in the range whose limiting viscosity [eta] is 0.01-20 deciliters/g is offered. Moreover, although this invention added the organoaluminium compound to the bottom of existence of this precuring catalyst, or this precuring catalyst, it offers under existence the manufacture approach of the polyolefine which was chosen from the alpha olefin of carbon numbers 2-20, the annular olefin, and the styrene monomer and which is characterized for a kind by the polymerization or copolymerizing at least.

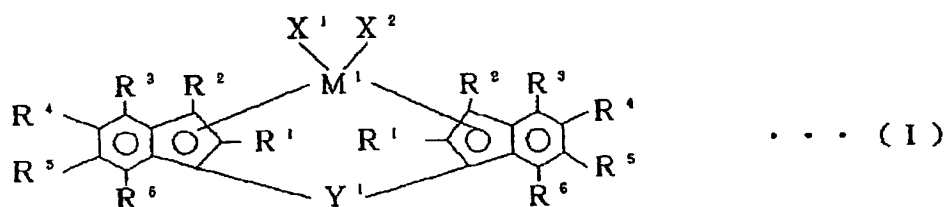
[0011]

[Embodiment of the Invention] A kind chosen as a catalyst used for precuring in the manufacture approach of this invention from the transition-metals compounds of the 4th group of the periodic table who has the (A) cyclopentadienyl group, (B) (B-1) The thing which was chosen as the ionicity compound list which reacts with an aluminum oxy compound and the ((B-2) A) above-mentioned transition-metals compound, and can be changed into a cation from clay (B-3), the clay mineral, and the ion-exchange nature stratified compound and which contains a kind at least is used. A kind chosen, for example from a component (A-1), a following component (A-2), and (A-3) a following component as a transition-metals compound of the 4th group of the periodic table who has the indenyl group of the above-mentioned (A) component can be mentioned.

(A-1) Component : (A-1) a component is a general formula (I).

[0012]

[Formula 4]



[0013] R1 -R6 shows the hydrocarbon group of a hydrogen atom, a halogen atom, and carbon numbers 1-20, or the halogen content hydrocarbon group of carbon numbers 1-20 independently among [type, respectively. R3 R4 and R4 R5 And R5 R6 It may join together mutually and a lot at least may form a ring. inside -- X1 And X2 The hydrocarbon group of a hydrogen atom, a halogen atom, or carbon numbers 1-20 is shown independently, respectively. Y1 the radical of the bivalence which combines two ligands -- it is -- the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, germanium, or a tin content radical -- being shown -- M1 Titanium, a zirconium, or a hafnium is shown.] It comes out and is the transition-metals compound expressed.

[0014] It sets to a general formula (I) and is R3. R4 and R4 R5 And R5 R6 The inner transition-metals compound with which the lot formed the ring at least is a compound known as a BASF mold complex. It sets to said general formula (I), and is R1 -R6. Chlorine, a bromine, a fluorine, and an iodine atom are mentioned as an inner halogen atom. As a hydrocarbon group of carbon numbers 1-20, for example Alkyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, n-hexyl group, and n-decyl group, The radical which aralkyl radicals, such as aryl groups, such as a phenyl group, 1-naphthyl group, and 2-naphthyl group, and benzyl, etc. were mentioned, and was permuted as a halogen content hydrocarbon group of carbon numbers 1-20 by the halogen atom with one or more pieces suitable for the hydrogen atom of the above-mentioned hydrocarbon group is mentioned. This R1 -R6 The radical which may differ even if mutually the same, and adjoins, i.e., R3, R4 and R4 R5 And R5 R6 A lot at least needs the inner thing for which it joins together mutually and the ring is formed. As an indenyl group in which such a ring was formed, 4, 5-benzoindenyl group, alpha-acenaphtho indenyl group, the alkylation object of the carbon numbers 1-10, etc. can be mentioned, for example.

[0015] Moreover, X1 And X2 Inside, as a halogen atom, chlorine, a bromine, a fluorine, and an iodine atom are mentioned and aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, tert-butyl, and n-hexyl group, and a phenyl group, and benzyl, etc. are mentioned as a hydrocarbon group of carbon numbers 1-20, for example. X1 And X2 It may be mutually the same or you may differ. On the other hand, it is Y1. It is the radical of the bivalence which combines two ligands. As a hydrocarbon group of the bivalence of the carbon numbers 1-20 of them for example, methylene group; -- dimethyl methylene group; -- alkylene groups, such as 1, 2-ethylene; dimethyl -1, 2-ethylene; 1, 4-tetramethylen radical; 1, and 2-cyclo propylene radical, -- Aryl alkylene groups, such as a diphenylmethylene radical, etc. are mentioned and a chloroethylene radical, a chloro methylene group, etc. are mentioned as a halogen content hydrocarbon group of the bivalence of carbon 1-20, for example. Moreover, as a silicon content radical of bivalence, a methyl silylene radical, a dimethyl silylene radical, a diethyl silylene radical, a diphenyl silylene radical, a methylphenyl silylene radical, etc. are mentioned, for example. Furthermore, as a germanium content radical and a tin content radical, the radical which changed silicon into germanium and tin can be mentioned in the above-mentioned silicon content radical. In addition, Y1 Although two ligands combined are usually the same, you may change with cases.

[0016] As a transition-metals compound expressed with the general formula (I) of this (A-1) component, the compound indicated by JP,6-184179,A, JP,6-345809,A, etc. can be mentioned, for example. As an example rac-dimethylsilane diyl-bis--1- The 2-methyl -4, (5-benzoindenyl)-zirconium dichloride, rac-phenylmethyl silane diyl-screw -1 -(2-methyl -4, 5-benzoindenyl)-Zirconium dichloride, rac-ethane diyl-bis--1- The 2-methyl -4, (5-benzoindenyl)-zirconium

dichloride, rac-butane diyl-screw -1 -(2-methyl -4, 5-benzoindenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- (4 and 5-benzoindenyl)-zirconium dichloride, rac-dimethylsilane diyl-screw -1 -(2-methyl-alpha-methyl-alpha-acenaphtho indenyl)- Zirconium dichloride, rac-phenylmethyl silane diyl-bis--1- What permuted the zirconium in benzoindenyl molds, such as (2-methyl-alpha-acenaphtho indenyl)-zirconium dichloride, or acenaphtho indenyl mold compounds, and these compounds by titanium or the hafnium can be mentioned.

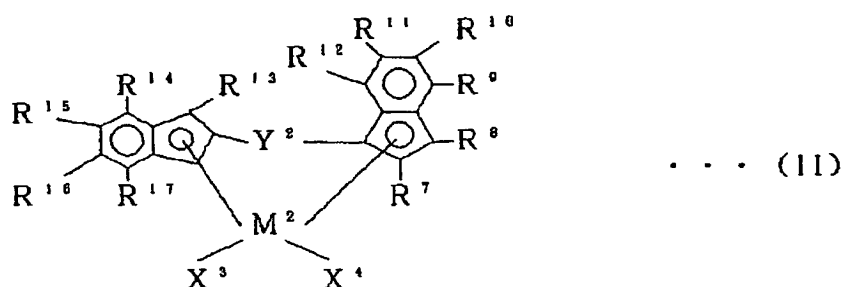
[0017] Furthermore, it sets to said general formula (I), and a component (A-1) is R3. R4 and R4 R5 And R5 R6 Any group is the transition-metals compound which has 4, 5 and 6 corresponding to the transition-metals compound or it which has the indenyl frame which does not form the ring, and a 7-tetrahydro indenyl frame. This transition-metals compound is a compound known as a Hoechst mold complex. As a transition-metals compound of this (A-1) component, the compound indicated by JP,4-268308,A, a 5-306304 official report, a 6-100579 official report, the 6-157661 official report, the 7-149815 official report, the 7-188318 official report, the 7-258321 official report, etc. can be mentioned, for example.

[0018] As an example Dimethylsilane diyl-bis--1- (2-methyl-4-phenyl indenyl)-zirconium dichloride, Dimethylsilane diyl-screw-1-[2-methyl-4- Indenyl]-zirconium dichloride, (1-naphthyl) Dimethylsilane diyl-bis--1- (2-ethyl-4-phenyl indenyl)-zirconium dichloride, dimethylsilane diyl-bis--1-[2-ethyl-4-(1-naphthyl) indenyl] zirconium dichloride, phenylmethyl silane diyl-bis--1- (2-methyl-4-phenyl indenyl)-zirconium dichloride, phenylmethyl silane diyl-bis--1-[2-methyl-4-(1-naphthyl) indenyl]-zirconium dichloride, phenylmethyl silane diyl-bis--1- Aryl substitution products, such as (2-ethyl-4-phenyl indenyl)-zirconium dichloride and phenylmethyl silane diyl-bis--1-[2-ethyl-4-(1-naphthyl) indenyl]-zirconium dichloride, rac-dimethyl silylene-bis--1- (2-methyl-4-ethyl indenyl)-zirconium dichloride, rac-dimethyl silylene-screw -1 -(2-methyl-4-isopropyl indenyl)- Zirconium dichloride, rac-dimethyl silylene-bis--1- (2-methyl-4-tertiary butyl indenyl)-zirconium dichloride, rac-phenylmethyl silylene-screw -1 -(2-methyl-4-isopropyl indenyl)- Zirconium dichloride, rac-dimethyl silylene-bis--1- (2-ethyl-4-methyl indenyl)-zirconium dichloride, rac-dimethyl silylene-screw -1 -(2, 4-dimethyl indenyl)- Zirconium dichloride, rac-dimethyl silylene-screw -1 -(2-methyl-4-ethyl indenyl)- At least 2, such as zirconium dimethyl, and 4- Substitution product, rac-dimethyl silylene-bis--1- (4 and 7-dimethyl indenyl)-zirconium dichloride, rac-1, and 2-ethane diyl - bis--1-(2-methyl -4, 7-dimethyl indenyl)-zirconium dichloride and rac-dimethyl silylene-bis--1- (3 and 4 --) 7-trimethyl indenyl-zirconium dichloride, rac-1 and 2-ethane diyl - bis--1-(4, 7-dimethyl indenyl)-zirconium dichloride, rac-1, and 2-butane diyl - bis--- at least 2, 4, and 7- at least 4, such as -1-(4, 7-dimethyl indenyl)-zirconium dichloride, and 7- At least 3, 4, and 7- Or a substitution product, dimethylsilane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, phenylmethyl silane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, rac-1, 2-ethane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-diphenyl silane diyl-bis--1- The 2-methyl -4, (6-diisopropyl indenyl)-zirconium dichloride, rac-phenylmethyl silane diyl-screw -1 -(2-methyl -4, 6-diisopropyl indenyl)- Zirconium dichloride, rac-dimethylsilane diyl-bis--1- At least 2, such as (2, 4, and 6-trimethyl indenyl)-zirconium dichloride, 4, and 6- is a substitution product and a rac-dimethylsilane diyl-screw. - 1 -(2, 5, 6-trimethyl indenyl)- At least 2, such as zirconium dichloride, 5, and 6- Substitution product, rac-dimethyl silylene-screw - (2-methyl -4, 5 and 6, and 7-tetrahydro 1-indenyl)-zirconium dichloride, rac-ethylene-screw -(2-methyl - 4, 5, 6, 7-tetrahydro-1-indenyl)- Zirconium dichloride, rac-dimethyl silylene-screw - (2-methyl -4, 5 and 6, and 7-tetrahydro-1-indenyl)-zirconium dimethyl, rac-ethylene-screw (2-methyl - 4, 5, 6, 7-tetrahydro-1-indenyl)-zirconium dimethyl, rac-ethylene-screw - 4, 5 and 6, such as (4, 7-dimethyl -4, 5 and 6, and 7-tetrahydro-1-indenyl)-zirconium dichloride, a 7-tetrahydro indenyl compound, etc., And what permuted the zirconium in these compounds by titanium or the hafnium can be mentioned.

(A-2) Component : (A-2) a component is a general formula (II).

[0019]

[Formula 5]

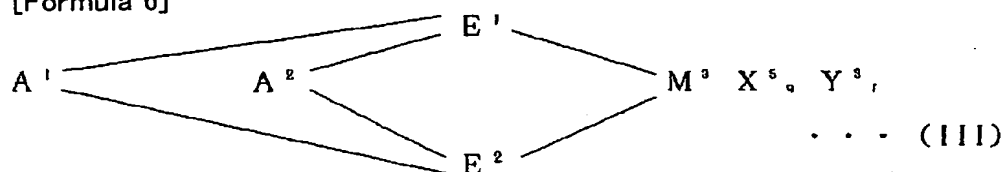


[0020] R7 -R13, R15, R16 and X3, and X4 show a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently among [type, respectively, it may join together mutually and R7 and R8 may form a ring. R14 and R17 show a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical independently, respectively. Y2 It is the radical of the bivalence which combines two ligands. The hydrocarbon group of carbon numbers 1-20, The halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, a germanium content radical, -O-, -CO-, -S-, -SO2-, -NR18-, --18-, -P(O)R18-, -BR18-, or -AlR18- is shown, and R18 shows a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, and the halogen content hydrocarbon group of carbon numbers 1-20. M2 Titanium, a zirconium, or a hafnium is shown.] It comes out and is the transition-metals compound expressed.

[0021] This transition-metals compound is a single bridge formation mold complex. It sets to said general formula (II), and is R7 -R13, and R15, R16 and X3. And X4 Chlorine, a bromine, a fluorine, and an iodine atom are mentioned as an inner halogen atom. As a hydrocarbon group of carbon numbers 1-20, for example Alkyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, n-hexyl group, and n-decyl group, Aralkyl radicals, such as aryl groups, such as a phenyl group, 1-naphthyl group, and 2-naphthyl group, and benzyl, etc. are mentioned. As a halogen content hydrocarbon group of carbon numbers 1-20 The radical permuted by the halogen atom with one or more pieces suitable for the hydrogen atom of the above-mentioned hydrocarbon groups, such as trifluoromethyl, is mentioned. As a silicon content radical, as an oxygen content radical, a methoxy group, an ethoxy radical, etc. are mentioned, a thiol group, a sulfonic group, etc. are mentioned, a trimethylsilyl radical, a dimethyl (t-butyl) silyl radical, etc. are mentioned, and a phenyl phosphine radical etc. is mentioned [a dimethylamino radical etc. is mentioned and] as a Lynn content radical as a nitrogen content radical as a sulfur content radical. Moreover, R7 R8 It may join together mutually and rings, such as a fluorene, may be formed. The radical excluding a hydrogen atom from what was mentioned in the above R7 - R13 grade as an example of R14 and R17 is mentioned. As R7 and R8, a hydrogen atom and a with a carbon number of six or less alkyl group are desirable, a hydrogen atom, a methyl group, an ethyl group, an isopropyl group, and a cyclohexyl radical are more desirable, and a hydrogen atom is still more desirable. Moreover, R9, R12, R14 And as R17, a with a carbon number of six or less alkyl group is desirable, a methyl group, an ethyl group, an isopropyl group, and a cyclohexyl radical are more desirable, and an isopropyl group is still more desirable. R10, R11, R13, R15 And as R16, a hydrogen atom is desirable. X3 X4 If it carries out, a halogen atom, a methyl group, an ethyl group, and a propyl group are desirable.

[0022] Y2 As an example, methylene, ethylene, ethylidene, isopropylidene, Cyclohexylidene, 1, 2-cyclo hexylene, dimethyl silylene, Tetramethyl disilylene, dimethylgermirene, methyl BORIRIDEN (CH3-B=), Methyl aluminum RIDEN (CH3-aluminum=), phenyl HOSUFIRIDEN (Ph-P=), Phenyl phospho RIDEN (PhPO=), 1, 2-phenylene, vinylene (-CH=CH-), There are vinylidene (CH2 =C=), methyl imide, oxygen (-O-), sulfur (-S-), etc., and methylene, ethylene, ethylidene, and isopropylidene are desirable in respect of the object achievement of this invention also in these.

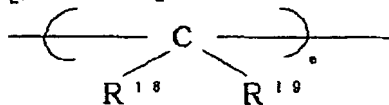
[Formula 6]



[0027] Moreover, X3 As an example of the sigma bond nature ligand shown, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20, the aryloxy group of carbon numbers 6-20, the amide group of carbon numbers 1-20, the silicon content radical of carbon numbers 1-20, the phosphide radical of carbon numbers 1-20, the sulfide radical of carbon numbers 1-20, the acyl group of carbon numbers 1-20, etc. are mentioned. this X3 the case where there are more than one -- two or more X3 even when it is the same -- differing -- **** -- other X3, E1, and E2 Or Y2 The bridge may be constructed. On the other hand, it is Y3. Amines, ether, phosphines, thioether, etc. can be mentioned as an example of a Lewis base shown. this Y3 the case where there are more than one -- two or more

Y3 even when it is the same -- differing -- **** -- other Y3 E1 and E2 Or X5 The bridge may be constructed. Next, A1 And A2 As a bridge formation radical which consists of a with a carbon numbers of one or more shown hydrocarbon group, it is a general formula [0028], for example.

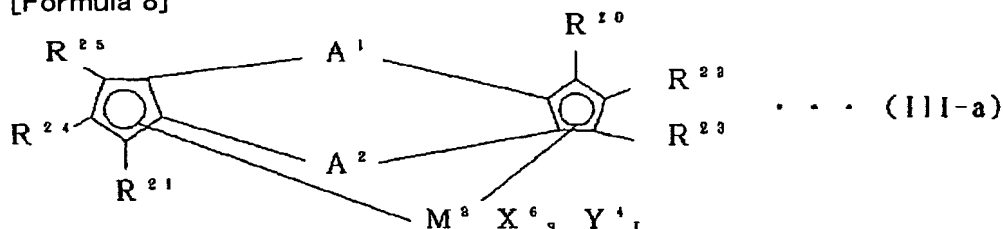
[Formula 7]



[0029] (R18 and R19 are a hydrogen atom or the hydrocarbon group of carbon numbers 1-20, respectively, even if mutually the same, you may differ, and it may join together mutually, and they may form the ring structure.) e shows the integer of 1-4. What is expressed is mentioned and a methylene group, ethylene, an ethylidene radical, a propylidene radical, an isopropylidene radical, a cyclohexylidene radical, 1, 2-cyclohexylene radical, a vinylidene radical ($\text{CH}_2=\text{C}=\cdot$), etc. can be mentioned as the example. In these, a methylene group, ethylene, and an isopropylidene radical are suitable. This A1 And A2 You may differ, even if mutually the same. This general formula (III) It sets to the transition-metals compound expressed, and is E1. And E2 It is A1 when it is a substituent cyclopentadienyl group, an indenyl group, or a permutation indenyl group. And A2 Association of a bridge formation radical may be a duplex (2 (1 1') 2') bridge formation mold, and may be a duplex (2 (1 2') 1') bridge formation mold. Such a general formula (III) In the transition-metals compound expressed, it is a general formula (III-a).

[0030]

[Formula 8]



[0031] The transition-metals compound which comes out and makes a ligand the duplex bridge formation mold bis(cyclopentadienyl) derivative expressed is desirable. In the above-mentioned general formula (III-a), M3, A1, A2, and q and r are the same as the above. X6 the ligand of ** sigma bond nature -- being shown -- X6 the case where there are more than one -- two or more X6 even when it is the same -- differing -- **** -- other X6 Or Y4 The bridge may be constructed. This X6 As an example, it is a general formula (III). X5 The same thing as what was illustrated by explanation can be mentioned. Y4 a Lewis base -- being shown -- Y4 the case where there are more than one -- two or more Y4 even when it is the same -- differing -- **** -- other Y3 Or X4 The bridge may be constructed. As this example of Y4, it is a general formula (III). Y3 The same thing as what was illustrated by explanation can be mentioned. Although R20-R25 show a hydrogen atom, a halogen atom, the hydrocarbon group of carbon numbers 1-20, the halogen content hydrocarbon group of carbon numbers 1-20, a silicon content radical, or a hetero atom content radical, respectively, at least one of them needs not to be a hydrogen atom. Moreover, even if R20-R25 are mutually the same, they may differ from each other, and adjoining radicals may join together mutually and they may form the ring.

[0032] The ligands of the transition-metals compound which makes a ligand this duplex bridge formation mold bis(cyclopentadienyl) derivative may be any of a duplex (2 (1 1') 2') bridge formation mold and (1 2') (2 1') a duplex bridge formation mold. This general formula (III) As an example of a transition-metals compound expressed (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-isopropylidene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-

ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (3-methyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (4, 5-benzoidenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4, 5-benzoidenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (4-isopropyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4-isopropyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (5, 6-dimethyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (5, 6-dimethyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-ethylene) screw (4, 7-diisopropyl indenyl) zirconium dichloride, - (2 (1 and 1'-ethylene) and 2'-ethylene) screw (4, 7-diisopropyl indenyl) Zirconium dichloride, (4-phenyl indenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (4-phenyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-ethylene) screw (3-methyl-4-isopropyl indenyl) zirconium dichloride, (3-methyl-4-isopropyl indenyl) (1 and 1'-ethylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (5, 6-benzoidenyl) (1, 2'-ethylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (5, 6-benzoidenyl) (1 and 1'-ethylene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-ethylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-ethylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1, 2'-methylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-isopropylidene) A (2 and 2'-methylene)-screw Zirconium dichloride, (Indenyl) (1 and 1'-methylene) (2 and 2'-methylene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-isopropylidene) (2 and 2'-isopropylidene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-propylidene) (2 and 2'-propylidene) (3-methylcyclopentadienyl) Zirconium dichloride, (Cyclopentadienyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-methylene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-ethylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-ethylene) (2 and 2'-isopropylidene)-screw (3-methylcyclopentadienyl) zirconium dichloride, - (2 (1 and 1'-methylene) and 2'-methylene) screw (3-methylcyclopentadienyl) zirconium dichloride (2 (1 and 1'-methylene) and 2'-ISO), A propylidene-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1 and 1'-ethylene) A (2 and 2'-methylene)-screw Zirconium dichloride, - (2 (1 and 1'-ethylene) and 2'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1 and 1'-methylene) A (2 and 2'-methylene)-screw Zirconium dichloride, - (2 (1 and 1'-methylene) and 2'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1 and 1'-isopropylidene) A (2 and 2'-isopropylidene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-methylene) screw (3-methylcyclopentadienyl) zirconium dichloride, - (2 (1, 2'-ethylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-isopropylidene) A (2 and 1'-isopropylidene)-screw Zirconium dichloride, (3-methylcyclopentadienyl) (1, 2'-ethylene) A (2 and 1'-methylene)-screw Zirconium dichloride, - (2 (1, 2'-ethylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1, 2'-methylene) A (2 and 1'-methylene)-screw Zirconium dichloride, - (2 (1, 2'-methylene), 1'-isopropylidene) screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, (3, 4-dimethylcyclopentadienyl) (1, 2'-isopropylidene) What permuted zirconiums in these compounds, such as (2 and 1'-isopropylidene)-screw (3, 4-dimethylcyclopentadienyl) zirconium dichloride, by titanium or the hafnium can be mentioned. Of course, it is not limited to these.

[0033] The catalyst used for precuring in this invention as a transition-metals compound of the (A) component preferably Although at least two sorts chosen from the aforementioned (A-1) component (the BASF mold complex or the Hoechst mold complex), the component (A-2) (single bridge formation mold complex), and (A-3) the component (duplex bridge formation mold complex) are used Especially, the combination of a zirconium compound-hafnium compound, a zirconium compound-zirconium compound, and a hafnium compound-hafnium compound is suitable.

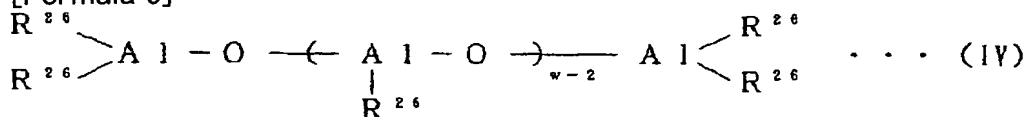
[0034] As an example with such suitable combination A single bridge formation mold zirconium complex-single bridge formation mold hafnium complex, a BASF mold zirconium complex-BASF mold hafnium complex, a Hoechst mold zirconium complex-Hoechst mold hafnium complex, a single bridge formation mold zirconium complex-BASF mold hafnium complex, A single bridge formation mold zirconium complex-Hoechst mold hafnium complex, a BASF mold zirconium complex-single bridge formation mold hafnium complex, a Hoechst mold zirconium complex-single bridge formation mold hafnium complex, the -two-fold BASF mold zirconium complex bridge formation mold hafnium complex, A -two-fold Hoechst mold zirconium complex bridge formation mold hafnium complex, -two-fold single bridge formation mold zirconium complex bridge formation mold hafnium complex, -two-fold duplex bridge formation mold zirconium complex bridge formation mold hafnium complex, and duplex bridge formation mold zirconium complex-BASF mold hafnium catalyst, A duplex bridge formation mold zirconium complex-Hoechst mold hafnium catalyst, a duplex bridge formation mold zirconium complex-single bridge formation mold hafnium complex, a single bridge formation mold zirconium complex-single bridge formation mold zirconium complex, a BASF mold zirconium complex-BASF mold zirconium complex, A Hoechst mold zirconium complex-Hoechst mold zirconium complex, a BASF mold zirconium complex-single bridge formation mold zirconium complex, a Hoechst mold zirconium complex-single bridge formation mold zirconium complex, the -two-fold BASF mold zirconium complex bridge formation mold zirconium complex, The -two-fold Hoechst mold zirconium complex bridge formation mold zirconium complex, a duplex bridge formation mold zirconium complex-single bridge formation mold zirconium complex, a -two-fold duplex bridge formation mold zirconium complex bridge formation mold zirconium complex, a single bridge formation mold hafnium complex-single bridge formation mold hafnium complex, A BASF mold hafnium complex-BASF mold hafnium complex, a Hoechst mold hafnium complex-Hoechst mold hafnium complex, a BASF mold hafnium complex-single bridge formation mold hafnium complex, a Hoechst mold hafnium complex-single bridge formation mold hafnium complex, The -two-fold BASF mold hafnium complex bridge formation mold hafnium complex, the -two-fold Hoechst mold hafnium complex bridge formation mold hafnium complex, a duplex bridge formation mold hafnium complex-single bridge formation mold hafnium complex, a -two-fold duplex bridge formation mold hafnium complex bridge formation mold hafnium complex, etc. are mentioned.

[0035] (A) the case where the combination of a zirconium compound and a hafnium compound is used as a transition-metals compound of a component -- the content of the zirconium compound in a mixed transition-metals compound -- desirable -- 1-99-mol % -- more -- desirable -- 2-95-mol % -- further -- desirable -- 5-90-mol % -- it is the 10-80-mol range of % especially preferably.

[0036] in the catalyst used for a precuring catalyst in this invention, it was chosen from the ionicity compound which reacts with an aluminum (B-1) oxy compound and said (B-2) transition-metals compound, and can be changed into a cation as a (B) component and (B-3) clay, the clay mineral, and the ion-exchange nature stratified compound -- a kind is used at least. As an aluminum oxy compound of the above-mentioned (B-1) component, it is general formula (IV)

[0037].

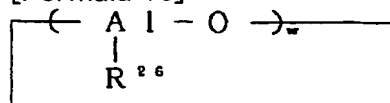
[Formula 9]



[0038] the inside of a formula, and R26 -- carbon numbers 1-20 -- desirable -- a hydrocarbon group or halogen atoms, such as an alkyl group of 1-12, an alkenyl radical, an aryl group, and an arylated alkyl radical, -- being shown -- w -- average degree of polymerization -- being shown -- usually -- 2-50 -- it is the integer of 2-40 preferably. in addition, every -- even if R26 is the same, it may differ. The chain-like aluminosilicate shown and general formula (V)

[0039]

[Formula 10]



... (V)

[0040] (-- R26 and w are the same as the thing in said general formula (IV) among a formula.) -- the annular aluminosilicate shown can be mentioned. What is necessary is for there to be especially no definition about the means, and just to make it react according to a well-known approach, although the method of contacting alkylaluminum and condensing agents, such as water, is mentioned as a manufacturing method of said aluminosilicate. For example, there is an approach to which dissolve ** organoaluminum compound in the organic solvent, add the organoaluminum compound at the beginning at the time of the approach of contacting this in water, and ** polymerization, make trialkylaluminum react to the approach and ** tetra-ARUKIRUJI aluminosilicate to which the water of crystallization contained in the approach of adding water behind, ** metal salt, etc. and the water of adsorption to an inorganic substance or the organic substance are made to react with an organoaluminum compound, and water is made to react further. In addition, as aluminosilicate, you may be the thing of toluene insolubility.

[0041] One sort of these aluminum oxy compounds may be used, and they may be used combining two or more sorts. Although anything can be used if it is the ionic compound which reacts with said transition-metals compound and can be changed into a cation as a component (B-2) on the other hand General formula of the point of being able to form the polymerization active spot efficiently especially to a degree (VI) (VII) ([L1-R27] h+) a b ([Z]-) ... (VI) ([L2] h+) ... (VII) (however, L2 is M5, R28R29M6, R303 C, or R31M6.) a b ([Z]-) L1 among [(VI) and a formula (VII) Lewis base and [Z]- the anion to which two or more radicals combined non-ligating property anion [Z1] - with the element, i.e., [M4 G1 G2 ..., -- Gf] or here [[Z2]- and here] -- [Z1]- (here -- it is -- M4 -- the 5-15th group element of the periodic table -- the 13-15th group element of the periodic table is shown preferably.) G1 -Gf A hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-20, the dialkylamino radical of carbon numbers 2-40, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the aryloxy group of carbon numbers 6-20, the alkyl aryl radical of carbon numbers 7-40, the arylated alkyl radical of carbon numbers 7-40, the halogenation hydrocarbon group of carbon numbers 1-20, the acyloxy radical of carbon numbers 1-20, an organic metalloid radical, or the hetero atom content hydrocarbon group of carbon numbers 2-20 is shown, respectively. G1 -Gf Two or more may form the ring inside. f shows the integer of [(valence of the central metal M4) +1]. [Z2]- the logarithm of the inverse number of an acid dissociation constant (electric dissociation exponent) -ten or less Brønsted acid -- the conjugate base of the combination of independent or Brønsted acid, and Lewis acid or the conjugate base generally defined as super-strong acid is shown. Moreover, the Lewis base may configure. Moreover, R27 shows a hydrogen atom, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, an alkyl aryl radical, or an arylated alkyl radical, and, as for a cyclopentadienyl group, a substituent cyclopentadienyl group, an indenyl group or a fluorenyl group, and R30, R28 and R29 show the alkyl group, the aryl group, alkyl aryl radical, or arylated alkyl radical of carbon numbers 1-20, respectively. R31 shows large annular ligands, such as a tetra-phenyl porphyrin and a phthalocyanine. In the ionic valence of [L1-R27] and [L2], h is the integer of 1-3 and a is one or more integers and b= (hxa). M5 The periodic table 1-3rds, 11-13, and 17 group element are included, and it is M6. The 7-12th group element of the periodic table is shown.] It can come out and what is expressed can be used suitably.

[0042] Here, it is L1. As an example Ammonia, monomethylamine, an aniline, dimethylamine,

diethylamine, N-methylaniline, a diphenylamine, N,N-dimethylaniline, a trimethylamine, triethylamine, tree n butylamine, a methyl diphenylamine, a pyridine, p-BUROMO-N, N-dimethylaniline, p-nitro -Amines, such as N and N-dimethylaniline, Nitril, such as ester, such as thioether, such as phosphines, such as a triethyl phosphine, triphenyl phosphine, and diphenylphosphine, and tetrahydrothiophene, and ethyl benzoate, an acetonitrile, and a benzonitrile, can be mentioned.

[0043] As an example of R27, hydrogen, a methyl group, an ethyl group, benzyl, a trityl radical, etc. can be mentioned, and a cyclopentadienyl group, a methylcyclopentadienyl radical, an ethylcyclopentadienyl radical, a pentamethylcyclopentadienyl group, etc. can be mentioned as an example of R28 and R29. As an example of R30, a phenyl group, p-tolyl group, p-methoxyphenyl radical, etc. can be mentioned, and tetraphenylporphine, a phthalocyanine, an allyl compound, metallyl, etc. can be mentioned as an example of R31. M5 [moreover,] as an example -- Li, Na, K, Ag, Cu, Br, I, and I3 etc. -- it can mention -- M6 Mn, Fe, Co, nickel, Zn, etc. can be mentioned as an example.

[0044] (Moreover, [Z1]-, i.e., [M4 G1 G2, ... It sets to Gf] and is M4. As an example, B and aluminum are preferably mentioned for B, aluminum, Si, P, As, Sb, etc.) Moreover, G1 and G2 -Gf As an example As a dialkylamino radical, a dimethylamino radical, a diethylamino radical, etc., As an alkoxy group or an aryloxy group, a methoxy group, an ethoxy radical, an n-butoxy radical, a phenoxy group, etc., As a hydrocarbon group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, n-octyl radical, n-ray KOSHIRU radical, a phenyl group, p-tolyl group, benzyl, a 4-t-buthylphenyl radical, 3, 5-dimethylphenyl radical, etc., As a halogen atom, as a fluorine, chlorine, a bromine, iodine, and a hetero atom content hydrocarbon group p-fluoro phenyl group, 3, a 5-difluoro phenyl group, a pentachlorophenyl group, 3 and 4, 5-trifluoro phenyl group, a pentafluorophenyl radical, 3, 5-screw (trifluoromethyl) phenyl group, a screw (trimethylsilyl) methyl group, etc., A pentamethyl antimony radical, a trimethylsilyl radical, a trimethyl gel mill radical, a diphenyl arsine radical, a dicyclohexyl antimony radical, diphenyl boron, etc. are mentioned as an organic metalloid radical.

[0045] moreover It is the conjugate base of the combination of the Broensted acid independent not more than -10 or Broensted acid, and Lewis acid [Z2]. - As an example, the anion, i.e., electric dissociation exponent, of non-ligating property ** trifluoro methansulfonic acid anion () [CF3] SO3-, screw (trifluoromethane sulfonyl) methyl anion, screw (trifluoromethane sulfonyl) benzyl anion, screw (trifluoromethane sulfonyl) amide, and perchloric acid anion (ClO4) -, a trifluoroacetic acid anion () CF3 CO2-, a hexafluoro antimony anion () SbF6-, a fluorosulfonic acid anion () [FSO3] -, a chlorosulfonic-acid anion () [ClSO3] -, a fluorosulfonic acid anion / 5-antimony fluoride (FSO3 / SbF5) -, a fluorosulfonic acid anion / 5-fluoride arsenic (FSO3 / AsF5) -, trifluoro methansulfonic acid / 5-antimony fluoride () [CF3SO3] /SbF5- etc. -- it can mention.

[0046] As an example of such (B-2) a component compound Tetra-phenyl triethyl borate ammonium, tetra-phenyl boric acid tree n-butyl ammonium, tetra-phenyl boric acid trimethylammonium, tetra-phenyl boric acid tetraethylammonium, tetra-phenyl methyl borate (tree n-butyl) ammonium, Tetra-phenyl boric acid benzyl Ammonium, tetra-phenyl boric acid dimethyl diphenyl ammonium, tetra-phenyl boric acid triphenyl (methyl) ammonium, tetra-phenyl trimethyl borate anilinium, tetra-phenyl methyl borate pyridinium, (Tree n-butyl) Tetra-phenyl boric acid benzyl pyridinium, tetra-phenyl methyl borate (2-cyano pyridinium), Tetrakis Triethyl borate ammonium, (Pentafluorophenyl) Tetrakis Boric acid tree n-butyl ammonium, tetrakis (pentafluorophenyl) boric acid triphenyl ammonium, tetrakis (pentafluorophenyl) boric acid tetra-n-butyl ammonium, tetrakis (Pentafluorophenyl) Boric acid tetraethylammonium, tetrakis (pentafluorophenyl) boric acid benzyl (tree n-butyl) ammonium, tetrakis (pentafluorophenyl) methyl borate diphenyl ammonium, tetrakis (Pentafluorophenyl) Boric acid triphenyl (Pentafluorophenyl) Ammonium, tetrakis (Methyl) Methyl borate anilinium, tetrakis (pentafluorophenyl) boric acid dimethyl anilinium, tetrakis (pentafluorophenyl) trimethyl borate anilinium, tetrakis (pentafluorophenyl) methyl borate pyridinium, (Pentafluorophenyl) Tetrakis (pentafluorophenyl) boric acid benzyl pyridinium, tetrakis (pentafluorophenyl) methyl borate (2-cyano pyridinium), Tetrakis (pentafluorophenyl) boric acid benzyl (2-cyano pyridinium), Tetrakis

(Pentafluorophenyl) Methyl borate Tetrakis (4-cyano pyridinium) Boric acid triphenyl phosphonium, tetrakis [screw (3, 5-ditrifluoromethyl) phenyl] boric acid dimethyl anilinium, tetraphenyl boric acid ferro SENIUMU, tetra-phenyl boric acid silver, tetra-phenyl boric acid trityl, (Pentafluorophenyl) Tetra-phenyl boric acid tetra-phenyl porphyrin manganese, tetrakis (pentafluorophenyl) boric acid ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid (1 and 1'-dimethyl ferro SENIUMU), Tetrakis (pentafluorophenyl) boric acid decamethyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid silver, Tetrakis Boric acid trityl, tetrakis (Pentafluorophenyl) A boric acid lithium, tetrakis (Pentafluorophenyl) Sodium borate, tetrakis (Pentafluorophenyl) (Pentafluorophenyl) Boric acid tetra-phenyl porphyrin manganese, silver tetrafluoborate, silver hexa-fluorophosphate, silver hexafluoroarsenate, silver perchlorate, silver tri-fluoroacetate, silver methanesulfonate, etc. can be mentioned.

[0047] One sort of ionicity compounds which are this (B-2) component and which react with the transition-metals compound of a ** (A) component, and can be changed into a cation may be used, and may be used combining two or more sorts. (B-3) As a component, clay, a clay mineral, or an ion-exchange nature stratified compound is used. Clay is the aggregate of a fine water silicate mineral, when a suitable quantity of water is mixed and kneaded, and plasticity is produced and it gets dry, rigidity is shown, and matter which will be sintered if it burns by high temperature is said. Moreover, a clay mineral means the water silicate which makes a clayey principal component. The field constituted by ionic bond etc. is the compound which takes the crystal structure piled up to parallel by the weak coupling force mutually, and an ion-exchange nature stratified compound means what has the exchangeable ion to contain. Most clay minerals are ion-exchange nature stratified compounds. Artificial composition of these may be carried out not only in a natural thing. As an ion-exchange nature stratified compound, the ion join character compound which has the **** structure of the shape of a layer, such as for example, a roppo maximum dense packing mold, an anti MOMON mold, a cadmium chloride mold, and a cadmium iodide mold, can be mentioned.

[0048] (B1 3) As an example of a component, a kaolin, a bentonite, kibushi clay, gairome clay, an allophane, a HISHINGERU stone, pyrophyllite, talc, a micaceous group, a montmorillonite group, a vermiculite, a chlorite group, a palygorskite, nacrite, dickite, halloysite, etc. are mentioned. (B-3) A thing 0.3-5ml [/g] or more has pore volume with a radius of 20A or more measured with the method of mercury penetration especially desirable as a component 0.1ml /or more. Moreover, it is also desirable to perform a chemical treatment from the impurity clearance in clay or structure, and the point of change of a function. Here, a chemical treatment puts both the surface treatment which removes the impurity which is acting to the front face as the ** person, and **** which affects the clayey crystal structure. Specifically, acid treatment, alkali treatment, salts processing, organic substance ****, etc. are mentioned. Acid treatment removes a surface impurity, and also increases surface area by making cations, such as aluminum in the crystal structure, iron, and magnesium, eluted. In alkali treatment, the clayey crystal structure is destroyed, moreover it brings about change of clayey structure, by salts processing and organic substance processing, ion complex, a molecular complex, organic complex, etc. can be formed, and surface area, the distance between layers, etc. can be changed. ion-exchange nature -- using -- the exchangeable ion of **** -- another ** -- also obtaining the matter between layers in the condition that between layers was expanded by permuting by high ion -- it is -- last ** It is also possible to still secure the polymerization reaction field in which a main catalyst exists into between layers.

[0049] What could use the above-mentioned (B-3) component as it was, and could use what newly carried out addition adsorption of the water, or carried out **** dehydration ***** may be used. (B-3) As a component, a desirable thing is clay or a clay mineral, and the most desirable thing is a montmorillonite. (B1 3) As for a component, it is desirable to process with a silane system compound and/or an organoaluminium compound. Activity may improve by this processing. As this silane system compound, for example Trialkylsilyl chloride, such as trimethylsilyl chloride, triethyl silyl chloride, triisopropylsilyl chloride, tert-butyl dimethylsilyl chloride, tert-butylphenylsilyl chloride, and phenethyl dimethylsilyl chloride Dimethylsilyl dichloride, diethyl silyl dichloride, diisopropyl silyl dichloride, bis-diphenethyl silyl dichloride,

methyl phenethyl silyl dichloride, diphenyl silyl dichloride, dimesitylsilyl dichloride, Dialkyl silyl dichloride, such as JITORIRU silyl dichloride, methyl silyl trichloride, Alkyl silyl trichloride, such as ethyl silyl trichloride, isopropyl silyl trichloride, phenyl silyl trichloride, mesityl silyl trichloride, tolyl silyl trichloride, and phenethyl silyl trichloride And the halide which replaced the part of the above-mentioned chloride by other halogens A screw An amine, a screw (Trimethylsilyl) An amine, a screw (Triethyl silyl) An amine, a screw (dimethyl ethyl silyl) amine, a screw (diethyl methyl silyl) amine, a screw (dimethylphenyl silyl) amine, a screw (dimethyl tolyl silyl) amine, a screw (dimethyl mesityl silyl) amine, (Triisopropyl silyl) Silylamine, such as N and N 1 dimethylamino trimethyl silane, a trimethyl (diethylamino) silane, and N-(trimethylsilyl) imidazole The poly silanols called by the trivial name of par alkyl polysiloxy polyol Silanols, such as a tris (trimethylsiloxy) silanol Silylamide **, such as N, O-screw (trimethylsilyl) acetamide, a screw (trimethylsilyl) trifluoro acetamide, N-(trimethylsilyl) acetamide, a screw (trimethylsilyl) urea, and a trimethylsilyl diphenylurea, Cyclosiloxanes, such as straight chain-like siloxanes, such as 1 and 3-dichloro tetramethyl disiloxane, and a pentamethyl cyclopentane siloxane Tetraalkylsilanes, such as a dimethyl diphenyl silane, a diethyl diphenyl silane, and a diisopropyl diphenyl silane A trimethyl silane, a triethyl silane, a triisopropyl silane, Trialkyl silanes, such as a tree t 1 butyl silane, a triphenyl silane, a tritolyl silane, a TORIMESHI chill silane, a methyl diphenyl silane, dinaphthyl methylsilane, and screw (diphenyl) methylsilane Inorganic silicon compounds, such as tetrachlorosilane and silicon tetrabromide, are mentioned. It is silylamine preferably among these and is trialkyl silane chloride more preferably. Although one kind of silane system compound may be used from the inside of these, it is also possible to use for arbitration combining two or more kinds depending on the case.

[0050] Furthermore, although there is especially no limit as an organoaluminium compound used for processing of a component (B-3), the meeting object of the annular aluminosilane or annular aluminosilane expressed with the straight chain-like aluminosilane or the above-mentioned general formula (V) expressed with the alkyl group content aluminium compound expressed with the general formula (VIII) mentioned later and the same formula, for example and the above-mentioned general formula (IV) can be used preferably. In seashell body, trialkylaluminums, such as trimethylaluminum, triethylaluminum, TORIPURO pill aluminum, triisobutylaluminum, and tree t-butyl aluminum, Halogens, such as dimethyl aluminum chloride, diethyl ARUMIUMU chloride, a dimethyl aluminum methoxide, a diethyl aluminum methoxide, dimethyl aluminum hydroxide, and diethyl aluminum hydroxide, an alkoxy group Or the alkylaluminum of hydrogen atom content, such as alkylaluminum of hydroxyl-group content, a dimethyl aluminum hydride, and a diisobutyl aluminum hydride, It is aluminosilane, such as methyl aluminosilane, ethyl aluminosilane, and isobutyl aluminosilane, etc., and especially trimethylaluminum or triisobutylaluminum is [among these] desirable. (B-3) One sort of organoaluminium compounds used for processing of a component may be used from the inside of these, and may be used combining two or more sorts.

[0051] (B-3) Although there is no limit in ** about the operating rate of the silane system compound and organoaluminium compound which are used for processing of a component, when a component (B1 3) is clay or a clay mineral It is the rate that 0.1-100000 mols of silicon original hands in a silane system compound usually become 0.5-10000 mols preferably to one mol of hydroxyl groups in a component. (B-3) Moreover, when using organic aluminum-ized ****, 0.1-100000 mols of aluminum atoms in an organoaluminium compound are usually used at a rate which becomes 0.5-10000 mols preferably. Moreover, it is the rate that the silicon atom in a silane system compound is set to 0.001-100g to 1g (B-3) of components when a component (B-3) is except clay or a clay mineral, and when using an organoaluminium compound, it uses at a rate that the aluminum atom in an organoaluminium compound is set to 0.001-100g, and things are desirable. If out of range, there is a thing which is the above-mentioned rate and which polymerization activity falls. (B-3) Processing of a component may be performed in inert gas, such as nitrogen, or hydrocarbons, such as a pentane, a hexane, toluene, and a xylene. Furthermore, it is desirable to carry out between the boiling points of a room temperature to an activity solvent especially during the boiling point of an activity solvent from -30 degrees C as well as the ability to perform this processing under polymerization temperature.

[0052] In the polymerization catalyst in this invention, as this (B) component, a component (B-1),

a component (B-2), and a component (B-3) may be used independently, and you may use combining these. the case where a compound is used for the operating rate of (A) catalyst component and (B) catalyst component in this precuring catalyst as a (B) catalyst component (B-1) -- a mole ratio -- desirable -- 1:1-1:106 -- more -- desirable -- 1:10-1:104 The range is desirable, and when deviating from the above-mentioned range, the catalyst cost per unit weight polymer becomes high, and is not practical. (B-2) the case where a compound is used -- a mole ratio -- desirable -- 10:1-1:100 -- the range of 2:1-1:10 is more preferably desirable. When deviating from this range, the catalyst cost per unit weight polymer becomes high, and it is not practical. moreover, the case where clay or a clay mineral is used as a compound (B-3) -- the mole ratio of the hydroxyl group in (A) catalyst component and (B) catalyst component -- desirable -- 1:0.1-1:100000 -- the range of 1:0.5-1:10000 is more preferably desirable. Furthermore, when an ion-exchange nature stratified compound is used as a compound (B-3), the operating rates of (A) catalyst component and (B) catalyst component are 1:1-1:100000 preferably in a weight ratio. When deviating from this range, the catalyst cost per unit weight polymer becomes high, and it is not practical.

[0053] Furthermore, the catalyst used for precuring in this invention may contain the aforementioned (A) component and the (B) component as a principal component, and is (A). The (C) organoaluminium compound and/or support may be contained as a principal component in a component and (B) component list. As for this support, it is desirable to use it, when a catalyst is what does not contain a component as a (B) component (B-3).

[0054] Here, as an organoaluminium compound of the (C) component, it is general formula (VIII) $R_{32}vAlQ_3-v$. The compound shown by ... (VIII) (R_{32} shows the alkyl group of carbon numbers 1-10 among a formula, Q shows a hydrogen atom, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, or a halogen atom, and v is the integer of 1-3) is used. Said general formula (VIII) As an example of the compound shown, trimethylaluminum, triethylaluminum, triisopropyl aluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminium chloride, methyl aluminum dichloride, ethyl aluminum dichloride, a dimethyl aluminum fluoride, a diisobutyl aluminum hydride, a diethyl aluminum hydride, ethylaluminium sesquichloride, etc. are mentioned. Preferably, they are trimethylaluminum, triethylaluminum, and triisobutylaluminum. One sort of these organoaluminium compounds may be used and they may be used combining two or more sorts. moreover, the operating rate of (A) catalyst component and the (C) organoaluminium compound used by request -- a mole ratio -- desirable -- 1:1-1:20000 -- more -- desirable -- 1:5-1:2000 -- the range of 1:10-1:1000 is still more preferably desirable. Although the polymerization activity per 1g of transition-metals compounds can be raised by using an organoaluminium compound, while an organoaluminium compound becomes useless when, and deviating especially from the above-mentioned range, it may remain so much in a polymer, and when few, sufficient catalytic activity may not be acquired, and it may not be desirable. [too much]

[0055] In this invention, even if there are few each catalyst components, a kind can be supported and used for suitable support. (C) Although there is especially no limit about the class of support of a component and both inorganic oxide support the other inorganic support and organic support can be used, the inorganic oxide support from a point or the other inorganic support of mol HOROJI-control is especially desirable. Specifically as inorganic oxide support, it is SiO_2 , aluminum $2O_3$, MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , and CaO , ZnO , BaO and ThO_2 . Such mixture, for example, a silica alumina, a zeolite, a ferrite, glass fiber, etc. are mentioned. Especially in these, it is SiO_2 . Or aluminum $2O_3$ It is desirable. In addition, the above-mentioned inorganic oxide support may contain a small amount of carbonate, a nitrate, a sulfate, etc.

[0056] on the other hand -- as support other than the above -- $MgCl_2$ and $Mg(OC_2H_5)_2$ etc. -- general formula $MgR_{33}X_7$ y represented with a magnesium compound etc. The magnesium compound expressed, its complex salt, etc. can be mentioned. Here, R_{33} is the alkyl group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20 or the aryl group of carbon numbers 6-20, and X_7 . The alkyl group of a halogen atom or carbon numbers 1-20 is shown, $0-2y$ are 0-2, and x is $x+y=2$. every -- R_{33} and every -- X_7 respectively -- being the same -- moreover, it may differ or you may be. Moreover, as organic support, polymers, such as

a polystyrene and styrene-divinylbenzene copolymer, polyethylene, polypropylene, permutation polystyrene, and polyarylate, starch, carbon, etc. can be mentioned. as the support used in this invention -- MgCl_2 , MgCl (OC two H5), Mg (OC two H5) $_2$, SiO_2 , and aluminum 2O_3 etc. -- it is desirable. Moreover, although the description of support changes with the classes and processes, 10-200 micrometers of mean particle diameter are 1-300 micrometers usually 20-100 micrometers more preferably. If particle size is small, the fines in a polymer will increase, and if particle size is large, the big and rough particle in a polymer will increase, and it will become lowering of bulk density, and the cause of plugging of a hopper. moreover, the specific surface area of support -- usually -- $1-1000\text{m}^2 / \text{g}$ -- desirable -- $50-500\text{m}^2 / \text{g}$, and pore volume -- usually -- $0.1-5\text{cm}^3 / \text{g}$ -- they are $0.3-3\text{cm}^3 / \text{g}$ preferably.

[0057] When either specific surface area or pore volume deviates from the above-mentioned range, catalytic activity may fall. In addition, it can ask for specific surface area and pore volume from the volume of the nitrogen gas with which it adsorbed according to the BET adsorption method (J. refer to Am.Chem.Soc, the 60th volume, and the 309th page (1983)). Furthermore, as for the above-mentioned support, it is usually desirable to calcinate and use at 200-800 degrees C preferably 150-1000 degrees C. When [of a catalyst component] making said support support a kind at least, it is desirable from points, such as applicability to processes, such as MORUHO logy control and a vapor phase polymerization, to make both (A) catalyst component and (B) catalyst component support preferably either [at least] (A) catalyst component or (B) catalyst component.

[0058] About the approach of making this support supporting either [at least] the (A) component or the (B) component How to mix at least one side and support of ** (A) component and the (B) component, for example, although not restricted especially, ** After processing support with an organoaluminium compound or a halogen content silicon compound, How to mix with either [at least] the (A) component or the (B) component in an inert solvent, ** The approach to which support, the (A) component, the (B) component, its both and organoaluminium compound, or a halogen content silicon compound is made to react, ** Face the catalytic reaction of the approach of mixing with the (B) component or the (A) component, the approach of mixing the catalytic-reaction object of ** (A) component and the (B) component with support, ** (A) component, and the (B) component after making support support the (A) component or the (B) component. The approach of making support living together etc. can be used. In addition, the organoaluminium compound of the (C) component can also be added in the reaction of the above-mentioned **, **, and **.

[0059] Thus, after the acquired catalyst once performs solvent distilling off and takes it out as a solid-state, it may be used for precuring, and it may be used for precuring as it is. In this invention, 10-6 to ten - two mols of (A) components are usually preferably used per 1g of support in the amount of 3×10^{-6} to ten - three mols. Moreover, the operating rate of the (B) component [(B-1) a component, a component (B-2), and a component (B-3)] to the (A) component is as above-mentioned.

[0060] When the operating rate of a ** (B) component [(B-1) a component, a component (B-2), and a component (B-3)] and support or the operating rate of the (A) component and support deviates from the above-mentioned range, activity may fall. thus, the mean particle diameter of the prepared catalyst -- usually -- 2-500 micrometers -- desirable -- 10-400 micrometers -- especially -- desirable -- 20-200 micrometers -- it is -- specific surface area -- usually -- $20-1000\text{m}^2 / \text{g}$ -- it is $50-500\text{m}^2 / \text{g}$ preferably. When mean particle diameter is less than 2 micrometers, the fines in a polymer may increase, and when it exceeds 500 micrometers, the big and rough particle in a polymer may increase. When specific surface area is under $20\text{m}^2 / \text{g}$, activity may fall, and when $1000\text{m}^2 / \text{g}$ is exceeded, the bulk density of a polymer may fall. Thus, advantageous high bulk density and the polyolefine which has the outstanding particle size distribution can be industrially obtained by supporting to support.

[0061] The precuring catalyst of this invention is first manufactured under existence of said catalyst by [which carry out the polymerization of a kind at least] having been chosen out of the alpha olefin and annular olefin of carbon numbers 2-20. Here as an alpha olefin of carbon numbers 2-20 Ethylene, a propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-

octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, etc. are mentioned. As an annular olefin Cyclopentene, a cyclo heptene, norbornene, 5-ethyl-2-norbornene, tetracyclo dodecen, etc. are mentioned. As a polymerization format, you may be any of a batch process and continuous system, and the approach of arbitration can be adopted out of a slurry polymerization method, a vapor-phase-polymerization method, a bulk-polymerization method, a solution polymerization method, etc.

[0062] As a polymerization solvent used when carrying out a slurry polymerization or solution polymerization, halogenated hydrocarbon, such as aromatic hydrocarbon, such as alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Deccan, a dodecane, and kerosene, a cyclopentane, a cyclohexane, and a methylcyclohexane, benzene, toluene, and a xylene, ethylene chloride, a chlorobenzene, dichloromethane, and chloroform, etc. is mentioned, for example. These solvents may be used independently, and two or more sorts may be mixed and used. About polymerization conditions, the range of -20-150 degrees C of polymerization temperature is -50-200 degrees C usually 0-120 degrees C more preferably. the polymerization preassure force -- usually -- 0-200 kg/cm2 G -- desirable -- 0.1-150 kg/cm2 G -- 0.2-100kg/cm2 is the range of G more preferably. moreover, polymerization time amount -- usually -- it is the range of 1 minute - 10 hours more preferably for 30 seconds to 30 hours for 10 seconds to 40 hours. furthermore, the amount of the catalyst used -- a raw material monomer / (aforementioned A) component mole ratio -- desirable -- 1-108 -- more -- desirable -- 100-107 Choosing so that it may become is advantageous.

[0063] Moreover, a polymerization catalyst can be made to generate in this invention by performing support actuation to one [at least] support of the (A) component and the (B) component within a polymerization system. For example, said organoaluminium compound is further added as occasion demands with the (A) component and the (B) component, and support, and it is an olefin 0.1-50kg/cm2 In addition, the approach of performing precuring at -20-200 degrees C for 1 minute to about 40 hours, and making a catalyst particle generating can be used. The control (control of molecular weight) of the limiting viscosity of polyolefine made into the precuring catalyst generated by precuring or the object is said within the limits, and can perform the operating rate of each component of a polymerization catalyst, the amount of the polymerization catalyst used, polymerization temperature, the polymerization preassure force, etc. by selecting suitably.

[0064] The precuring catalyst acquired by such precuring is a per [in the range whose limiting viscosity [eta] is 0.1-20 deciliters/g / 1g of transition-metals compounds / 0.01-2000g] thing. Limiting viscosity [eta] is measured in the temperature of 135 degrees C among a tetralin solvent. While this limiting viscosity [eta] is inferior to melting workability in a polymerization or the polyolefine obtained by copolymerizing about an alpha olefin etc. ing, using this precuring catalyst in less than 0.01 deciliters /, if a mechanical strength is inadequate and g is exceeded in 20 deciliters /, the melt viscosity of the above-mentioned polyolefine will be high, and melting workability will fall. From fields, such as the melting workability of the above-mentioned polyolefine, and balance of a mechanical strength, as this limiting viscosity [eta], g is desirable in 0.05-20 deciliters /, and the range which is 0.1-18 deciliters/g is especially desirable.

[0065] Although the precuring catalysts acquired by precuring are per [0.01-2000g] 1g of transition-metals compounds of the (A) component, per [0.1-150g] 1g of transition-metals compounds are desirable, and they are desirable. [of 1-especially 120g]

[0066] The precuring catalyst manufactured by the above-mentioned precuring is a thing in the condition that the polymer adhered to the perimeter of a catalytic activity component, and this polymer and the catalyst are included in the reaction mixture after precuring termination. In this invention, this polymer and a catalyst (catalyst to which this polymer adhered when putting in another way) are called a precuring catalyst. the manufacture approach of this invention -- setting -- the bottom of existence of this precuring catalyst -- or it was chosen as the bottom of existence out of the alpha olefin, annular olefin, and styrene monomer of carbon numbers 2-20 although the organoaluminium compound was added as occasion demands -- polyolefine can be obtained for a kind a polymerization or by copolymerizing at least. Here, the same thing as the

above can be used as an organoaluminium compound. (A) the case where the operating rate of a catalyst component and the organoaluminium compound used by request is that in which said precuring catalyst does not contain an organoaluminium compound -- a mole ratio -- desirable -- 1:1-1:20000 -- more -- desirable -- 1:5-1:2000 -- the range of 1:10-1:1000 is still more preferably desirable. Moreover, although it changes with the amount used when said precuring catalyst is a thing containing an organoaluminium compound The mole ratio of the transition-metals compound in a precuring catalyst, and an organoaluminium compound, not using an organoaluminium compound at all 1:0.5-1:10000 and by using an organoaluminium compound in 1:2-1:8000 more preferably Although the polymerization activity per transition metals can be raised, while an organoaluminium compound becomes useless when, and deviating especially from the above-mentioned range, it may remain so much in a polymer, and when few, sufficient catalytic activity may not be acquired, and it may not be desirable. [not much]

[0067] The thing same as the alpha olefin of carbon numbers 2-20 and an annular olefin as the above is mentioned. moreover, as a styrene monomer Styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, 2, 4-dimethyl styrene, 2, 5-dimethyl styrene, 3, 4-dimethyl styrene, 3, 5-dimethyl styrene, 2 and 4, 5-trimethyl styrene, 2 and 4, 6-trimethyl styrene, Alkyl styrene, such as p-t-butyl styrene, p-chloro styrene, m-chloro styrene, o-chloro styrene, Halogenation styrene, such as p-bromostyrene, m-bromostyrene, o-bromostyrene, p-fluoro styrene, m-fluoro styrene, o-fluoro styrene, and o-methyl-p-fluoro styrene, etc. is mentioned.

[0068] A polymerization format and polymerization conditions can be made into the same thing as said precuring. moreover -- a block -- a pile -- the block copolymer of an olefin can also be lawfully manufactured more by different reaction condition from precuring. In this case, a different reaction condition is the following reaction step, after manufacturing the homopolymer of polypropylene first for example, using ** precuring catalyst. It is made to be the same as that of copolymerizing the monomer chosen from ethylene, the alpha olefin of carbon numbers 4-20, an annular olefin, and styrene, and a propylene, or the ** above-mentioned **. After copolymerizing the monomer and propylene which were chosen from ethylene, the alpha olefin of carbon numbers 4-20, an annular olefin, and styrene, It is manufacturing the block copolymer from which the preparation presentation of a monomer was changed at the following step, and the copolymerization presentation changed etc., and a monomer kind, polymerization temperature, a pressure, time amount, and a monomer brewing presentation are changed, and it points out performing a polymerization reaction in two or more steps.

[0069] The range of 50 degrees C or more of 60 degrees C or more of 70 degrees C or more of melting points of the polyolefine obtained by the approach of this invention is usually 80-160 degrees C still more preferably more preferably. In addition, this melting point is the value measured by the following approach. That is, after carrying out temperature up from a room temperature to 200 degrees C the rate for 10-degree-C/and holding for 3 minutes at 200 degrees C using a differential scanning calorimeter [the product made from SEIKO Electronic industry, and DSC200 mold], the temperature is lowered to 30 degrees C by part for 10-degree-C/. Carry out temperature up by part for 10-degree-C/, and let temperature of the fusion peak which appears in that case be the melting point, after holding for 5 minutes at 30 degrees C. As for this polyolefine, what has a melt index MI in the range for 0.005-1000g / 10 minutes is desirable. This MI has an inadequate melting fluidity in 0.005g / less than 10 minutes, and if it exceeds 1000g / 10 minutes, machine physical properties fall remarkably and are not desirable. From fields, such as balance of a melting fluidity and machine physical properties, more desirable MI is the range for 0.01-800g / 10 minutes, and its range for 0.05-600g / 10 minutes is especially desirable. In addition, this MI is ASTM. It is the value measured on the temperature of 230 degrees C, and the conditions of 2.16kg of loads based on D1238-T65.

[0070] For the melting tension MS of the above-mentioned polyolefine (g), the limiting viscosity [eta] (deciliter/g) measured in the temperature of 135 degrees C among the melting tension MS (g) measured in the temperature of 230 degrees C and a tetralin solvent is a formula.

$$\log MS \geq 3.17 \times \log [\eta] - 0.68 \quad (1)$$

It is desirable to fill *****. When logMS is smaller than the value of "3.17xlog[eta]-0.68", it is inferior to melting workability and the object of this invention is not reached. from the field of

UP, 11-292912A [TECHNICAL PROBLEM]
melting workability -- further -- desirable -- $\log MS \geq 3.17 \times \log[\eta] - 0.57$ -- desirable --
 $\log MS \geq 3.17 \times \log[\eta] - 0.46$ -- it is $\log MS \geq 3.17 \times \log[\eta] - 0.35$ especially preferably. The melting
tension MS is the value measured on condition that the following using the KYAPI log rough by
the Oriental energy machine company.

a part for capillary tube : 3.14m/ -- Temperature : [] -- in addition, 4000 weight ppm addition of
the 230 degrees C of the mixture of the weight ratio 1:1 of IRUGA NOx 1010 and BHT was
beforehand carried out as an antioxidant at the measurement sample. : The diameter of 2.095mm,
die length of 8.0mm, and 90 fluid inlet angles Diameter of a cylinder : 9.0mm Cylinder extrusion
rate : A part for 10mm/ Rolling-up rate

[0071] The bulk density of the above-mentioned polyolefine has desirable cc in 0.2-0.5g /, and
its cc is especially desirable in 0.3-0.5g /. In addition, bulk density is JIS. It asked based on
K6721.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Next, although an example explains this invention in more detail, this invention is not limited at all by these examples.

Preparation SiO227.1 (Fuji SHIRISHIA chemistry company make, trade name--10) g of n-heptane suspension of example of preparation 1 silica support methyl aluminoxane was heat-treated under the 2-hour nitrogen air current at 200 degrees C, and desiccation silica 25.9g was obtained. It was dropped with the dropping funnel, having covered 145.5ml of 1.5 mols [/.] methyl aluminoxane toluene solutions over this for 1.0 hours, having supplied this desiccation silica in 400ml of toluene cooled at -78 degrees C, and stirring it by dry ice / methanol bath. After leaving it in this condition for 4.0 hours, temperature up was carried out from -78 degrees C to 20 degrees C in 6.0 hours, and it was further left in this condition for 4.0 hours. Then, the reaction of a silica and methyl aluminoxane was made to complete by carrying out temperature up from 20 degrees C to 80 degrees C in 1.0 hours, and leaving it at 80 degrees C for 4.0 hours.

[0073] At 60 degrees C, twice, filtered this suspension at 60 degrees C, the obtained solid was carried out at 60 more degrees C by 400ml toluene, and washing was carried out by 400ml n-hexane. By carrying out reduced-pressure-drying processing of the solid after washing at 60 degrees C for 4.0 hours, silica support methyl aluminoxane 33.69g was obtained. The amount of support of methyl aluminoxane was 23.12 % of the weight. Thus, n-heptane was added to the obtained silica support methyl aluminoxane whole quantity, full capacity was made into 500ml, and suspension with a methyl aluminoxane concentration of 0.27 mols [/.] was prepared.

[0074] 9.26ml (methyl aluminoxane 2.5 millimol) of silica support methyl aluminoxane suspension obtained in the example 1 of preparation preparation of an example of preparation 2 silica support metallocene catalyst was extracted in the desiccation nitrogen-purge container, and 20ml of n-heptanes was added and stirred. To this suspension, as a transition-metals compound, toluene solution 5 micromole of rac-dimethylsilane diyl-bis--1-(2-methyl-4-phenyl indenyl) zirconium dichloride [rac-Me2 Si(2-Me-4-PhInd)2 ZrCl2], Toluene solution 5 micromole of rac-dimethylsilane diyl-bis--1-(2-methyl-4-phenyl indenyl) hafnium dichloride [rac-Me2 Si(2-Me-4-PhInd)2 HfCl2] was added, and it stirred at the room temperature for 0.5 hours. Then, the solid-state catalyst component which stopped stirring, and the solid-state catalyst component was made to sediment, and sedimented is light yellow, and it checked that a solution was transparent and colorless. Thus, the silica support metallocene catalyst was prepared.

[0075] After it heated the proof-pressure autoclave made from 1.4l. stainless steel with manufacture stirring equipment of an example 1 polypropylene system precuring catalyst at 80 degrees C and it fully carried out reduced pressure drying, it returned to the atmospheric pressure with desiccation nitrogen, 400ml [of desiccation deoxidation n-heptanes] and triisobutylaluminum (toluene solution) 0.5 millimol was supplied to this autoclave under the desiccation nitrogen air current, and it stirred for 10 minutes by 500rpm. The silica support metallocene catalyst prepared in the example 2 of preparation was thrown into this (they are ten micromole by the sum total of a zirconium compound and a hafnium compound), 8.0kg/cm2 of propylenes was continuously supplied by G, controlling at 30 degrees C, precuring was carried out for 90 minutes, and polypropylene (precuring catalyst) was obtained. Depressuring of the unreacted propylene was carried out after precuring termination, and nitrogen removed the

unreacted propylene further. When some obtained polypropylene was sampled under nitrogen-gas-atmosphere mind and the amount of precuring (the amount of polypropylene obtained by precuring) was calculated, it was 2620g per 1g of transition metals, and was 27.9g per 1g of silica support metallocene catalysts. Moreover, the limiting viscosity $[\eta]$ of the polypropylene obtained by precuring was 3.3 deciliters/g. The precuring catalyst acquired by precuring separated the solid-state part from the liquid part by the decantation, and saved it as a slurry of 100ml of desiccation deoxidation n-heptanes.

[0076] After it heated the proof-pressure autoclave made from 1.4l. stainless steel with manufacture stirring equipment of the polypropylene using an example 2 precuring catalyst at 80 degrees C and it fully carried out reduced pressure drying, it returned to the atmospheric pressure with desiccation nitrogen, 300ml [of desiccation deoxidation n-heptanes] and triisobutylaluminum (toluene solution) 0.5 millimol was supplied to this autoclave under the desiccation nitrogen air current, and it stirred for 10 minutes by 500rpm. 100ml (it is an equivalent for nine micromole by the zirconium and hafnium atom conversion) of precuring catalysts prepared in the example 1 was supplied to this, and temperature up was carried out to it to 70 degrees C. 8.0kg/cm² of propylenes was continuously supplied to this by G, and the polymerization was carried out for 30 minutes. Depressuring of the unreacted propylene was carried out after reaction termination, with the methanol of a large quantity, it deactivated, filtration desiccation processing of the catalyst was carried out, and polypropylene 189g was obtained. About this polypropylene, a melt index MI, limiting viscosity $[\eta]$, the melting tension MS, the melting point T_m, and bulk density were asked for and evaluated according to the approach indicated in the description text. A result is shown in the 1st table.

[0077] In the manufacture example 1 of an example 3 polyethylene system precuring catalyst, the propylene was changed into ethylene and polyethylene (precuring catalyst) was manufactured like the example 1 except having set polymerization time amount as for 45 minutes. When some obtained polyethylene was sampled under nitrogen-gas-atmosphere mind and the amount of precuring (the amount of polyethylene obtained by precuring) was calculated, it was 2740g per 1g of transition metals, and was 29.3g per 1g of silica support metallocene catalysts. Moreover, the limiting viscosity $[\eta]$ of the polyethylene obtained by precuring was 3.3 deciliters/g. The precuring catalyst acquired by precuring separated the solid-state part from the liquid part by the decantation, and saved it as a slurry of 100ml of desiccation deoxidation n-heptanes.

[0078] 184g of ethylene propylene rubbers was manufactured like the example 2 except having used what was prepared in the example 3 as manufacture precuring intermediation of the ethylene propylene rubber using an example 4 precuring polymerization catalyst.

[0079]

[A table 1]

第 1 表

	实施例 2	实施例 4
収量 (g)	1 8 9	1 8 4
MI (g/10分)	0. 3 5	0. 4 3
極限粘度 $[\eta]$ (dl/g)	2. 4 9	2. 5 9
融点 (°C)	1 4 7. 8	1 4 8. 0
高密度 (g/cc)	0. 4 5	0. 4 0
溶融張力 (g)	9. 0	6. 9

[Translation done.]

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